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(21) International Application Number: PCT/US98/15031 (22) International Filing Date: 21 July 1998 (21.07.98) (30) Priority Data: 08/897,968 21 July 1997 (21.07.97) US 08/926,159 9 September 1997 (09.09.97) US 09/012,382 23 January 1998 (23.01.98) US (63) Related by Continuation (CON) or Continuation-in-Part (CIP) to Earlier Application US 08/897,968 (CON) Filed on 21 July 1997 (21.07.97) (71) Applicant (for all designated States except US): AGUILA TECHNOLOGIES, INC. [US/US]; Suite 107, 310 Via Vera Cruz, San Marcos, CA 92069 (US). (72) Inventors; and (75) Inventors/Applicants (for US only): CAPOTE, M., Albert [US/US]; 4151 Parkside Place, Carlsbad, CA 92008 (US). ZHOU, Liqui [CN/US]; 845 Brooktree Lane #226, Vista, CA 92083 (US). ZHU, Xioqui [CN/US]; Apartment 158, 850 Brooktree Lane, Vista, CA 92083 (US). ZHOU, Zhim-	ing [CN/US]; 2425 Larpenteur Avenue #313, Maplewood, MN 55109 (US). (74) Agents: DILLAHUNTY, T., Gene et al.; Burns, Doane, Swecker & Mathis, L.L.P., P.O. Box 1404, Alexandria, VA 22313-1404 (US). (81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, HR, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>	
(54) Title: POLYMERIZABLE FLUXING AGENTS AND FLUXING ADHESIVE COMPOSITIONS THEREFROM		
(57) Abstract <p>A thermally curable adhesive composition that includes a fluxing agent that also acts as an adhesive is provided. The composition includes: (a) a fluxing agent represented by the formula RCOOH, wherein R comprises a moiety having two or more carbon-carbon double bonds wherein in one embodiment, at least one is within an acrylate or methacrylate group, and which may further contain at least one aromatic moiety; (b) a carboxylic acid neutralizing agent; (c) optionally, an effective amount of a cross-linkable diluent; (d) optionally, an effective amount of a source of free radical initiators; and (e) optionally, an effective amount of a resin. By employing an acrylate, methacrylate, or phenol in the structure of the adhesive flux, the cure temperature and moisture absorption characteristics can be significantly improved. The composition can be applied directly onto the surface(s) of devices that are to be joined electrically and mechanically. These devices include, printed circuit substrates, connectors, components, cables, and other electrical devices having metallization patterns to be soldered together by means of a solder-bumped pattern on one or both surfaces. Alternatively, a solder paste, comprising solder powder mixed with the fluxing agent of the present invention can be used. During the reflow step, the fluxing agent promotes wetting of the solder to the metallization patterns and, simultaneously, the fluxing agent itself cross-links to mechanically bond and encapsulate the surfaces and their metallizations. The compositions can also be used to formulate sinterable conductive ink.</p>		

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POLYMERIZABLE FLUXING AGENTS AND FLUXING ADHESIVE COMPOSITIONS THEREFROM

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FIELD OF THE INVENTION

This invention relates generally to electronic circuits and more particularly to electrical interconnection techniques.

BACKGROUND OF THE INVENTION

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In the assembly of electronic components, the solder bump interconnection method was developed to eliminate the expense, unreliability, and low productivity associated with manually wire bonding integrated circuit chips onto carrier or printed circuit substrates. The method utilizes solder bumps deposited on solder-wettable metal terminations on the chip and a matching pattern of solder-wettable terminations on the substrate. In the case of an upside down integrated circuit (flip chip), the flip chip is aligned to the substrate and all the joints are made simultaneously by melting the solder. Typically, the solder bumps are placed on the integrated circuit terminals while the chip is still in wafer form.

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To join the integrated circuit to the substrate, a flux, generally a no-clean, low residue flux, is placed on the substrate as a temporary adhesive to

hold the integrated circuit in place. The assembly is subjected to a solder melting thermal cycle in an oven or furnace thereby soldering the chip to the substrate. The surface tension of the solder aids to self align the chip to the substrate terminals. After this reflow step, removing the flux residue from
5 under the chip is difficult and requires sophisticated cleaning regimes. This is due, in part, to the close proximity of the chip to the substrate which typically is about 0.001 to 0.006 in. (25.4 to 150 μm). Therefore with conventional techniques the flux residues are generally left in the space between the chip and
the substrate. For this reason, the residues must be inert to prevent subsequent
10 corrosion of the assembly.

The next step in the assembly process is to encapsulate the chip which permits the use of polymeric substrates in flip chip assembly process. Encapsulation can result in significant improvements in the fatigue life of the solder bumps as compared to an unencapsulated flip chip assembly. The
15 technique of underfill encapsulation has gained considerable acceptance by the electronics industry and the materials of choice for underfill encapsulation have been epoxies. Polymeric substrate materials have higher coefficients of thermal expansion than that of a silicon chip, but the expansion coefficients of the underfill encapsulant epoxies can be adjusted with the addition of ceramic fillers
20 to reduce the level of thermal stress that develops between the substrate and the encapsulant.

Most underfill encapsulation procedures involve dispensing liquid encapsulants onto one or more edges of the flip chip assembly. Capillary action draws the encapsulant material through the minute gap between the chip
25 and the substrate. As is apparent, this underfill process can be quite slow due to the small dimensions. The gap must be completely filled and, after the epoxy is cured, be free of voids in order to provide adequate protection for the device and reduce fatigue of the solder joints. The flux residues remaining in

the gap reduce the adhesive and cohesive strengths of the underfill encapsulating adhesive.

As is apparent, the multi-step assembly process has a number of deficiencies. Furthermore, as the size of chips increases, the limiting effect of capillary action becomes more pronounced and renders the encapsulation procedure even more time consuming. As a result, it is expected that there will be a greater tendency for the epoxy polymer to separate from the ceramic filler during application. In addition, there will be more void spaces.

In an attempt to alleviate these problems associated with flip chip assembly, the industry has employed polymer flux compositions. Prior art polymer flux compositions suitable for assembling electronic components and particularly flip chips generally comprise an elaborate mixture comprising a thermosetting or thermoplastic resin, a flux activator that is generally halogenated, and a chemically protected curing agent which can also function as a fluxing agent. See, for example, U.S. Patents 5,088,189, 5,128,746, 5,136,365, 5,167,729, and 5,417,771, and EP 0 620 077 A1.

Prior art flux compositions containing thermosetting resins are undesirable due to their high viscosity and short shelf life which is typically less than one week. Moreover, conventional multi-component fluxing compositions are intrinsically not self-crosslinking. They require resins, such as epoxy resins, for crosslinking thereby further limiting the shelf life or pot life of the material and decreasing flux activity substantially. In addition, chemical protection of the carboxylic acid in the fluxing agent was essential to achieving stability and preventing premature reactions. This results in an acid that is functioning at much less than its full strength with the metal oxides.

As is apparent, the art is in search of more efficient chip assembly techniques that can consistently produce an essentially voidless underfill encapsulation. In particular, there is a need for a soldering flux that can

remove oxides and promote soldering without use of ionic or halogen-containing flux activators and that can serve as an adhesive to provide improved bonding at electrical interconnections.

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SUMMARY OF THE INVENTION

The present invention is based in part on the discovery of a thermally curable adhesive composition that comprises a fluxing agent that also acts as an adhesive. The composition includes: (a) a fluxing agent represented by the formula RCOOH , wherein R comprises a moiety having two or more carbon-carbon double bonds; (b) a carboxylic acid neutralizing agent; (c) optionally, an effective amount of a crosslinkable diluent; (d) optionally, an effective amount of a source of free radical initiators; and (e) optionally, an effective amount of a resin. In a preferred embodiment, at least one of the carbon-carbon double bonds in R is within an acrylate or methacrylate group. In another embodiment, R contains an aromatic moiety.

The composition can be applied directly onto the surface(s) of devices that are to be joined electrically and mechanically. These devices include, for example, printed circuit substrates, connectors, components, cables, and other electrical devices having metallization patterns to be soldered together by means of a solder-bumped pattern on one or both surfaces. Alternatively, a solder paste, comprising solder powder mixed with the fluxing agent of the present invention can be used. During the reflow step, the fluxing agent promotes wetting of the solder to the metallization patterns and, simultaneously, the fluxing agent itself crosslinks to mechanically bond and encapsulate the surfaces and their metallizations.

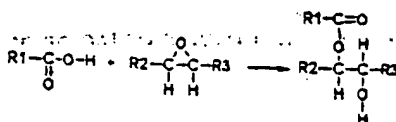
Unlike the polymer flux mixtures of the prior art, the inventive fluxing agent integrates within a single molecule a carboxylic acid group that provides

the fluxing action for the soldering process without need of corrosive ions or halogens, and polymerizable carbon-carbon double bonds that can polymerize upon application of heat, with or without the addition of free radical initiators, to form a high-strength solid adhesive polymer. This is accomplished without
5 generating gases, water, or other harmful by-products. Moreover, after the thermally curable adhesive composition is cured, the residues and any remaining fluxing agent do not need to be washed away or removed since they are non-corrosive. Because these residues are located permanently between the two surfaces joined together they do not interfere with test probes.

10 In a preferred embodiment, the fluxing agent contains acrylate or methacrylate groups which yields fast curing rates; their presence reduces the concentration of carboxylic acid and increases the hydrophobicity of the adhesives. In addition, the introduction of hydrophobic groups into the polymer backbone, such as aromatic or fluorine moieties, dramatically enhances the
15 water resistance.

In addition, any unreacted carboxylic acid from the fluxing agent after the fluxing reaction present in the high-strength solid adhesive polymer is neutralized by the action of the carboxylic acid neutralizer. This neutralization reaction eliminates the pendant acid groups which could promote electromigration of metals in humid environments if left unreacted.

25 Preferably, compounds that form the carboxylic acid neutralizing agent contain at least one epoxide moiety which reacts with the carboxyl group during the fluxing reaction that occurs during soldering. The epoxide consumes the carboxylic acid moiety by opening the epoxide three-member ring to form an ester and a hydroxyl group by the following reaction:



In the absence of a catalyst, the above reaction proceeds slowly at temperatures below about 180 °C with the reaction rate depending in part on the particular neutralizing agent. Therefore, the neutralizing agent does not interfere significantly with the fluxing activity of the fluxing agent.

5 The inventive thermally curable adhesive composition achieves good flux activity without the need for additional aggressive flux activators. The composition does not evolve gases that can create voids or bubbles in the composition during and after curing. Solvents are not required as the fluxing agent is itself a low viscosity liquid at soldering temperatures.

10 The adhesive strengths of the cured composition are comparable to the adhesion of copper cladding on FR4 epoxy printed circuit board laminates. Finally, the cured composition becomes a high corrosion resistant adhesive at high temperatures having a glass transition temperature above 150 °C and a coefficient of thermal expansion less than 80 ppm/°C. After being cured, the
15 thermally curable adhesive composition exhibits very low moisture absorption which minimizes the corrosion of the flip chip and reduces the tendency of the polymers to hydrolyze.

BRIEF DESCRIPTION OF THE DRAWINGS

20 As used herein, like reference numerals will designate similar elements in the various embodiments, wherein:

Figures 1 and 3 are each a cross sectional view of a device and substrate prior to attachment of the two surfaces to be interconnected;

25 Figures 2 and 5 are each a cross sectional view of the device and substrate surfaces after bonding; and

Figure 4 is a cross sectional view of a flip chip temporarily attached without solder reflow for testing or burn in prior to reflow.

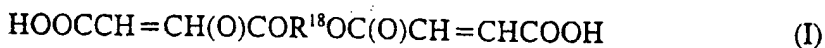
DETAILED DESCRIPTION OF THE INVENTION

The invention is directed to fluxing adhesive compositions that include a fluxing agent comprising a single active component which is capable of functioning as both a primary fluxing agent and a crosslinking monomer.

- 5 Generally, depending upon the intended end use, the inventive thermally curable adhesive composition comprises (a) a fluxing agent having a carboxylic acid group and one or more carbon-carbon double bonds, (b) a carboxylic acid neutralizing agent; (c) optionally, a crosslinkable diluent, (d) optionally, a free-radical initiator, and (e) optionally, a resin.

- 10 In addition the thermally curable adhesive composition may include a solvent for adjusting the viscosity. Other viscosity modifiers, thickeners and thixotropic agents may also be added. Fillers, such as silica powder, can be employed for increased modulus and lower thermal coefficient of expansion.

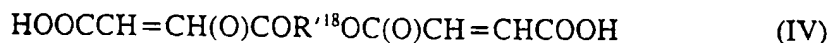
- 15 1. Fluxing Agents. The fluxing agent is a carboxyl containing compound that has the structure RCOOH , wherein R comprises a moiety which include two or more carbon-carbon double bonds. For high flux activity due to the presence of multiple carboxylic acids, the preferred fluxing agent is a carboxylic acid that is selected from the group consisting of compounds
20 represented by Formulae I, II, and III, and mixtures thereof.



- 25 wherein R^{18} is an alkyl having 1 to 16 carbons, preferably 1 to 9 carbons, and more preferably 1 to 3 carbons, wherein n is an integer from 1 to 16 preferably an integer from 1 to 9, and more preferably an integer from 1 to 3, wherein each of R^1 , R^2 , ... R^n , is independently selected from $-\text{C}(\text{O})\text{CH}=\text{CHCOOH}$, and H, wherein X^1 , X^2 , X^3 , and X^4 , are each independently selected from $-\text{CH}_2\text{OH}$,

-CH₂OC(O)CH=CHCOOH, and H, with the proviso that not all of X¹, X², X³, and X⁴ are H, and preferably only one of said X¹, X², X³, and X⁴ is H.

A preferred fluxing adhesive composition that has a lower curing temperature, faster curing rate and increased moisture resistance includes a
 5 fluxing agent that has the general structure R'COOH, wherein R' comprises a moiety having two or more carbon-carbon double bonds, of which preferably at least one is within an acrylate or methacrylate moiety, that is, R' contains at least one acrylate (-C(O)CH=CH₂) or methacrylate (-C(O)C(CH₃)=CH₂)
 group. (Preferably, there are 1 to 5 groups.) For high flux activity due to the
 10 presence of multiple carboxylic acids, a preferred fluxing agent is a carboxylic acid that is selected from the group consisting of compounds represented by Formulae IV, V, VI and mixtures thereof,



where R'¹⁸ is a substituted alkyl moiety containing at least one acrylate or methacrylate moiety and said substituted alkyl moiety comprising a chain having 1 to 16 carbons, preferably 1 to 9 carbons, and more preferably 1 to 3 carbons, and wherein n is an integer from 1 to 16, preferably an integer from 1
 20 to 9, and more preferably an integer from 1 to 3, wherein each of R'¹, R'², ...R'ⁿ, is independently selected from -C(O)CH=CHCOOH, -C(O)CH=CH₂, -C(O)C(CH₃)=CH₂, and H, and wherein Y¹, Y², Y³, and Y⁴, are each independently selected from -CH₂OH, -CH₂OCOCH=CH₂, -CH₂OCOC(CH₃)=CH₂, -CH₂OC(O)CH=CHCOOH and H with the proviso
 25 that not all of Y¹, Y², Y³, and Y⁴ are H, and preferably not more than one of said Y¹, Y², Y³, and Y⁴ is H.

Incorporating an acrylate and/or methacrylate in the structure can reduce the curing temperature of the adhesive polymer since the carbon-carbon double

bonds in the acrylate or methacrylate tend be more reactive than most other such double bonds. Reducing the crosslink temperature of the double bonds tends to make the adhesive flux more compatible with current practice in the field wherein solder reflow is achieved in a thermal cycle having a peak
5 temperature of 230°C. The lower crosslink temperature can produce an adhesive flux formulation that is fully crosslinked after only one or two passes through the solder reflow thermal cycle. The acrylate and methacrylate will also tend to repel moisture and reduce the absorption of water in the cured polymer. A particularly preferred acrylate containing fluxing agent is glycidyl
10 methacrylate which exhibits low viscosity, high flux activity and excellent curing characteristics, as further described in Example 4.

The fluxing agent typically comprises about 0.01%-100%, preferably about 5%-80%, and more preferably about 10%-70% by volume of the thermally curable adhesive composition.

15 The fluxing agents of the present invention exhibit flux activities that are superior to that of prior art polymer-fluxing agent mixtures. Since the inventive fluxing agents are intrinsically self-crosslinking, the thermally curable adhesive composition does not require the use of epoxy resins for crosslinking, though an epoxy may be used in the neutralizing agent. As a corollary, the
20 shelf life or pot life of the composition is long and its flux activity high relative to conventional polymer-fluxing mixtures that include epoxy resins.

Further, the adhesion properties, mechanical integrity, and corrosion resistance achieved with the fluxing agents are superior to those achieved with prior art polymer fluxing agents because there is no need to add aggressive
25 fluxing activators. The inventive fluxing agents are fully crosslinked and all components thereof are chemically immobilized upon curing. Even the reaction by-products of flux deoxidization of the metals may be chemically bound in the polymer matrix.

Carboxylic acids function well as fluxing agents to remove oxides from metals. In addition, carboxylic acids are also very effective crosslinking moieties when present in their reactive form in a fluxing composition containing a suitable thermosetting resin, such as an epoxy. For this reason, in the prior art, chemical protection of the carboxylic acid was essential to achieving stability and preventing premature reactions. Protection was achieved by binding the fluxing agent with a chemically- or thermally-triggered species so that it becomes reactive only at or near the time that the solder melts.

However, with the present invention, no such protection is necessary because the compositions can be formulated with only minimal amounts of components that can crosslink with the carboxylic acid moiety. This results in a fluxing agent that can function at near its full strength with the metal oxides to produce fluxing that is superior to any heretofore polymerizable fluxing agent. The flux activity of the inventive fluxing agent in some applications may be too high thereby requiring dilution of the fluxing agent to prevent formation of undesirable gaseous by-products.

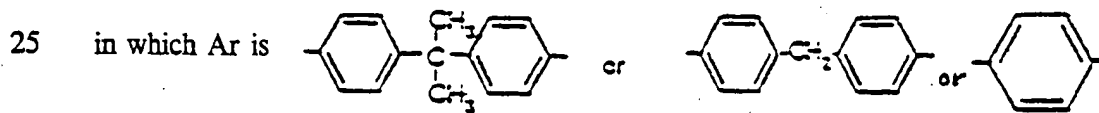
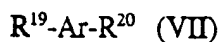
With the inventive fluxing agent, the principal crosslinking mechanism occurs at the carbon-carbon double bonds existing in the fluxing agent molecule and not at the carboxylic acid groups. The carboxylic acids do not react with the double bonds, therefore on its own, in the absence of other molecules that can react with the carboxylic acid, the fluxing agent does not polymerize at ambient temperatures. It is at elevated temperatures that the double bonds begin to open and react with other opened double bonds to crosslink. Since each fluxing agent molecule contains at least two double bonds, the molecules crosslink into polymeric networks.

By reducing or eliminating the need for a separate thermosetting resin in the flux composition, as is required in the prior art, the flux activity can be kept very high without concern about pre-maturely crosslinking the

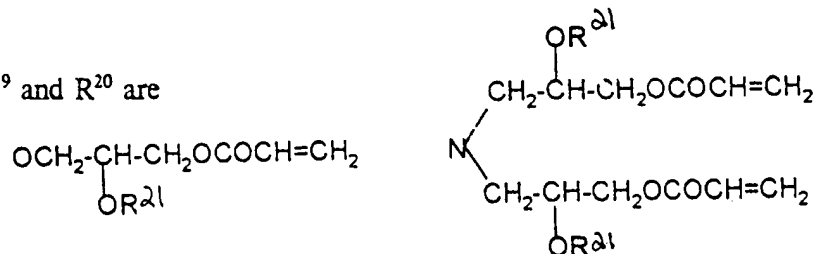
thermosetting resin. By crosslinking the fluxing agent itself, an adhesive having a higher glass transition temperature and lower coefficient of thermal expansion can be created without sacrificing fluxing activity.

Another preferred fluxing-adhesive composition, one that has very high moisture resistance, comprises a fluxing agent with the general structure $R''COOH$, wherein R'' comprises a moiety having two or more carbon-carbon double bonds, of which preferably at least one is within an acrylate or methacrylate moiety and R'' further contains at least one aromatic moiety, which is an unsaturated aromatic carbocyclic group having a single ring (e.g., phenyl) or multiple condensed rings (e.g., naphthyl) which condensed rings may or may not be aromatic. The aromatic moiety also includes substituted aromatic moieties. The R'' group can also be fluorinated. For high flux activity due to the presence of multiple carboxylic acids, the preferred fluxing agent is a carboxylic acid that is selected from the group consisting of compounds represented by Formulae VII and mixtures thereof. A particularly preferred aromatic-containing fluxing agent is one made from bisphenol A epoxy, as described in Example 1, which exhibits significant hydrophobicity.

The generalized structure for carboxylic acids containing two or more carbon-carbon double bonds and also containing aromatic moieties is:

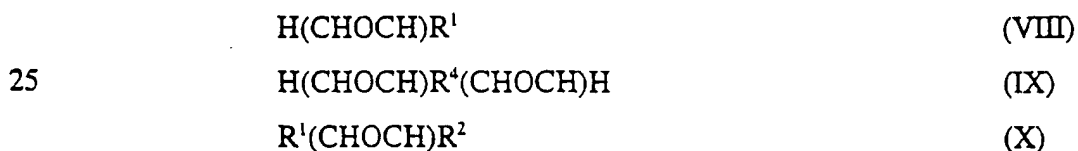


and R¹⁹ and R²⁰ are

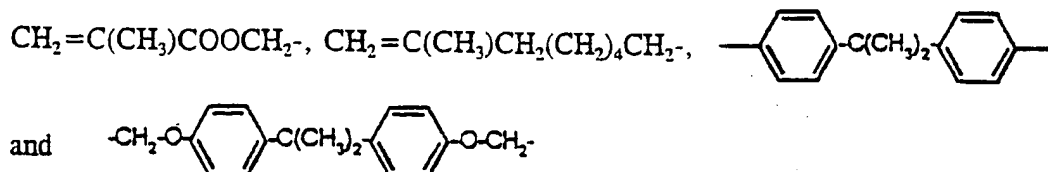


5 in which R²¹ is -C(O)CH=CH-COOH, -C(O)CF₂CF₂CF₂COOH, or H.

2. Carboxylic Acid Neutralizing Agent. The carboxylic acid neutralizing agent is a compound that has the structure R¹-X-R², wherein X comprises a carboxylic-neutralizing moiety such as, for example, epoxide, -NH- or -CH(OH)- group and wherein R¹ and R² are independently selected from (i) 10 H, (ii) alkyl or alkylene moiety having 1 to 18 carbons, preferably 1 to 9 carbons, and more preferably 1 to 3 carbons, and (iii) aromatic moiety which is an unsaturated aromatic carbocyclic group having a single ring (e.g., phenyl) or multiple condensed rings (e.g., naphthyl) which condensed rings may or may not be aromatic. The neutralizing agent may also be a compound containing 15 isocyanate or cyanate ester groups, or any other group that can react with the carboxylic acid. The aromatic moiety also includes substituted aromatic moieties. The alkyl, alkylene, or aromatic moieties can include one or more carbon-carbon double bonds and/or one or more of X groups. To neutralize the 20 carboxylic acids without the formation of condensation by-products, the preferred neutralizing agent is an epoxide that is selected from the group consisting of compounds represented by Formulae VIII, IX, and X, and mixtures thereof,



wherein R¹ and R² are defined above and R⁴ is preferably selected an alkyl, alkylene, or aromatic group. Preferably R¹, R², and R⁴ is selected from:



Another preferred neutralizing agent has the general structure

- 5 $\text{H}(\text{CHOCH})\text{R}^5$, wherein R^5 comprises a moiety having one or more carbon-carbon double bonds, of which preferably at least one is contained in an acrylate or methacrylate moiety, that is, R^5 contains at least one acrylate ($-\text{C}(\text{O})\text{CH}=\text{CH}_2$) or methacrylate ($-\text{C}(\text{O})\text{C}(\text{CH}_3)=\text{CH}_2$) group. (Preferably, there are 1 to 5 groups, for example, glycidyl methacrylate; 1,2-epoxy-7-octene; and
- 10 1,2-epoxy-9-decene.)

In the process of neutralizing the carboxylic acid of the fluxing agent, the neutralizing agent becomes incorporated, i.e., crosslinked, into the cured adhesive composition. Furthermore, incorporation an acrylate and/or methacrylate in the structure of the carboxylic neutralizing agent will also to

15 reduce the curing temperature of the adhesive polymer since the carbon-carbon double bonds in the acrylate or methacrylate tend to be more reactive than most other such double bonds. Reducing the crosslink temperature of the double bonds tends to make the adhesive flux more compatible with current practice in the field wherein solder reflow is achieved in a thermal cycle having a peak

20 temperature of 230°C. The lower crosslink temperature can produce an adhesive flux formulation that is fully crosslinked after only one or two passes through the solder reflow thermal cycle. The acrylate and methacrylate will also tend to repel moisture and reduce the absorption of water in the cured polymer. A particularly preferred acrylate containing neutralizing agent is

25 glycidyl methacrylate which exhibits low viscosity and high flux activity as further described in Example 4.

The amount of neutralizing agent employed is preferably proportional to the amount of fluxing agent present and the neutralizing agent typically

comprise about 0.01 %-90% preferably about 5 %-50%, and most preferably about 10 %-50% by volume of the thermally adhesive composition. Preferably, no more than a stoichiometric amount (with the carboxylic acid prior to fluxing reactions) is employed to neutralize the carboxylic acid in the fluxing agent.

- 5 Thermally curable adhesive compositions where the amount of neutralizing agent is substantially higher than the required stoichiometric amount will generally exhibit inferior fluxing properties, whereas compositions with substantially less than stoichiometric amounts of neutralizing agent will generally exhibit poor electrical insulation and high metallic electromigration
10 when exposed to humid environments.

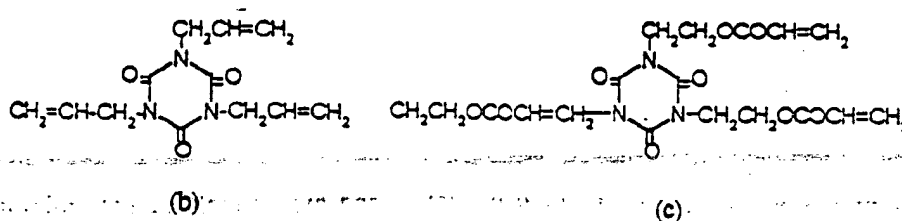
Since the neutralizing agents are chemically linked with the carboxylic acid in the fluxing agent only slowly and at elevated temperatures, they reduce the fluxing activity of the adhesive flux minimally. As a corollary, the shelf life or pot life of the composition is long and its flux activity high relative to
15 conventional polymer-fluxing mixtures that require epoxy resins.

With the inventive fluxing agent, the principal crosslinking mechanism still occurs at the carbon-carbon double bonds existing in the fluxing agent molecule and not at the carboxylic acid groups.

- 20 3. Diluents. The presence of carbon-carbon double bond(s) in the fluxing agent molecule allows much flexibility in the formulation of a flux composition with exceptional thermomechanical properties. This is achieved by the addition of double bond containing diluents that can also crosslink with the flux to create a superior adhesive. This technique permits the design of fluxing
25 adhesive compositions that can attain high crosslink densities, which are desirable for good thermomechanical properties and good adhesion. Moreover, this is accomplished without the concern of premature crosslinking and reduced pot life associated with the prior art. Preferred diluents include, for example,

(a) penta erythritol tetraacrylate, $C(CH_2OOCCH=CH_2)_4$, (b) triallyl-1,3,5-triazine-2,4,6 (1H,3H,5H)-trione, (c) tris[2-(acryloxy)ethyl]isocyanurate, (d) glycerol propoxylate triacrylate and mixtures thereof. Diluents (b) and (c) have the following structures:

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10

Other double bond compounds, many of which are commercially available, including, for example, diallyl phthalate and divinyl benzene can also be used. Hydrophobic diluents as described are preferred but hydrophilic diluents can also be employed when appropriate. The diluent when employed typically can comprise up to about 90%, preferably between about 5%-80%, and more preferably between about 50%-80% by volume of the thermally curable adhesive composition.

One benefit of employing hydrophobic diluents is that their presence tends to reduce the amount of water which the cured adhesive composition will absorb. The reason is that the fluxing agent, when crosslinked, will have active carboxylic groups that can attract water, even though these carboxylic groups, being part of a network, are immobile. Water acts as a plasticizer which softens the cured adhesive composition. The use of hydrophobic diluents which are crosslinked to the fluxing agent will counteract the hydrophilic effects of the carboxylic acid groups. Indeed, the cured adhesive compositions containing hydrophobic diluents can have less than 2% (wt) moisture when exposed to ambient conditions.

4. Free Radical Initiators. While the thermally curable adhesive composition can be cured using heat alone, the cross linking reaction can be initiated and facilitated by the presence of free-radicals, including, for example, those generated by benzoyl peroxide, butyl hydroperoxide, 2,2'-azobisisobutyronitrile, and mixtures thereof. These free radical initiators or sources are commercially available.

Free-radicals can be created *in-situ* by exposure of the free-radical initiator to heat, radiation, or other conventional energizing sources.

Introduction of an appropriate free-radical-initiator can accelerate the onset of crosslinking to the desired moment in a solder reflow operation. The presence of a small amount of free-radical crosslinking initiator in the fluxing agent can be used to control the rate and the temperature of crosslinking of the fluxing agent, ensuring effective fluxing action and strong adhesion of the fluxing agent to the substrates upon curing.

- 15 The free radical initiator when employed typically comprises up to about 5%, preferably between about 0%-3%, and more preferably about 0.3%-1% by weight of the thermally curable adhesive composition.

5. Resins. The thermally curable adhesive composition does not require resins; further, compositions that do not include resins tend to have longer pot lives and lower viscosities during solder reflow. However, as an option, a resin can be employed and it functions to increase the adhesion of the cured composition to the substrate and to increase the cohesive strength and glass transition temperature of the cured composition. The resin may be any suitable resin that is compatible (i.e., blendable) with the fluxing agent. By blendable is meant that the resins do not have to be chemically bonded to the fluxing agent and/or diluent. Resins which meet these requirements include, but are not limited to, epoxies, phenolics, novalacs (both phenolic and cresolic),

polyurethanes, polyimides, bismaleimides, maleimides, cyanate esters, polyvinyl alcohols, polyesters, and polyureas. Preferred resins 1,4-cyclohexanedimethanol diglycidyl ether, 3,4-epoxycyclohexylmethyl 3,4-epoxycyclohexanecarboxylate, N,N-diglycidyl-4-glycidyl-oxyaniline, bisphenol
5 A based epoxy resins, and mixtures thereof. These are commercially available.

Suitable compounds (including polymers) can also be modified to form resins that are blendable with the diluent and/or the carboxylic acid fluxing agent. Examples of such compounds are acrylics, rubbers (butyl, nitrile, etc.),
polyamides, polyacrylates, polyethers, polysulfones, polyethylenes,
10 polypropylenes, polysiloxanes, polyvinyl acetates/polyvinyl esters, polyolefins, cyanoacrylates, and polystyrenes. Generally, any compound can function as a resin if it can be modified to contain at least one of the following illustrative functional groups that act as reactive sites for polymerization: anhydrides, carboxylic acids, amides, amines, alcohols/phenols, nitriles, carbamates,
15 isocyanates, sulfonamides, semicarbazones, oximes, hydrazones, cyanohydrins, ureas, phosphoric esters/acids, thiophosphoric esters/acids, phosphonic esters/acids, phosphites, phosphonamides, and sulfonic esters/acids. For example, a polyolefin which has no reactive sites for binding and has poor adhesive properties is typically not a suitable resin, however, a carboxylated
20 polyolefin functions well when matched with a suitable crosslinking agent. A combination of these and other resins, such as non-crosslinkable thermoplastic resins, may also be used as resins. Resins when employed can comprise up to about 80%, preferably between about 10%-80%, and more preferably about 60%-70% by volume of the thermally curable adhesive composition.

25 In preparing the fluxing composition, the proportions of the five components may be varied over a considerable range and still yield acceptable fluxing activity as well as good post cured material properties. Preferably, the fluxing composition employed does not produce gaseous byproducts that can

result in the formation of bubbles in the final cured composition. This can be achieved with thermally curable adhesive compositions preferably formulated as follows:

- a) Fluxing agent comprising about 5%-80% (vol.) of the composition;
- 5 b) Neutralizing agent comprising about 0.1-90% (vol.) of the composition;
- c) Diluent comprising about 5%-80% (vol.) of the composition;
- d) Free radical initiator comprising about 0%-3% (wt) of the composition; and
- 10 e) Resin comprising about 0%-80% (vol.) of the composition.

It should be noted that some neutralizing agents can also function as resins. Therefore, when resins are employed, the amount can be kept to a minimum. Some thermally curable adhesive compositions having components within these ranges may exhibit undesirably high moisture absorption, low glass
15 transition temperatures, or high coefficients of thermal expansions after cured, but they remain useful as fluxing compositions in applications where these characteristics are not critical.

Most preferably, the thermally curable adhesive composition after being cured has a coefficient of thermal expansion of about 25 ppm/°C, a glass
20 transition temperature in excess of 150 °C, electrical insulation resistance greater than 100 MegOhms according to IPC-TM-650 testing on the IPC-B-24 test board and moisture content of less than 2%. These characteristics can be achieved with thermally curable adhesive compositions preferably comprising about 5%-35% (vol.) fluxing agent, a stoichiometric quantity of neutralizing
25 agent and about 20%-80% (vol.) diluent.

While, again, some of the fluxing agents within these ranges may exhibit high coefficient of thermal expansion or low glass transition temperature when

cured, they remain useful as fluxes in applications where these characteristics are not critical.

In order for the thermally curable adhesive composition to achieve the largest spreading and wetting by the solder, it must achieve and maintain low viscosity up to the temperature at which the solder melts and wets the metallizations. If the composition becomes too thick before the solder has melted, it will impede the flow of the solder melt and reduce the degree of metal soldering. For this reason, the curing of the composition must occur slowly relative to the time required to reach the melting point of the solder powder. This can be achieved by selection of the components with appropriate crosslinking temperatures and formulating the appropriate proportions by use of a differential scanning calorimeter to control reaction rates and times.

The thermally curable adhesive composition can also be used as a fluxing adhesive for use in sinterable conductive ink compositions that comprises:

- a) 1% to 65% (wt) of a high melting point metal or metal alloy powder, typically comprising Cu powder, however, other metals such as, for example, Ag, Au, Pt, Pd, Be, Rh, Ni, Co, Fe, Mo, and high-melting point alloys thereof;
- b) 6% to 65% (wt) of a low melting point metal or metal alloy powder (solder), typically comprising Sn, Bi, Pb, Cd, Zn, Ga, In, Hg, Sb, or an alloy thereof or other metal having a melting point that is lower than that of the high melting metal powder in part (a); and
- c) 5% to 50% (wt) of the thermally curable adhesive flux composition that also serves as a flux composition and as an adhesive.

Preferably the conductive ink composition comprises 13% to 65% (wt) of the high melting point metal, 6% to 29% (wt) of the low melting point

metal, and/or 5% to 35% (wt) of the thermally curable adhesive flux composition.

Techniques for employing electrically conductive compositions are described in U.S. Patents 5,376,403, 5,538,789, and 5,565,267 which are
5 incorporated herein. During the curing process of the sinterable conductive ink compositions, in order for the solder alloy to readily wet the other powder and sinter, the principal requirement of the thermally curable adhesive composition is that the polymers not harden before melting of the solder powder is achieved. Additionally, after curing, the composition must act as an adhesive that strongly
10 binds the cured ink composition to the printed circuit board substrate. The flux compositions of the instant invention are particularly suited for these applications.

METHODOLOGY

The thermally curable adhesive composition of the instant invention is
15 particularly suited for attaching flip chips to a substrate wherein the fluxing agent serves also as an encapsulating adhesive. The compositions eliminate the need for the additional assembly steps of washing the solder flux and then underfilling the chip-to-substrate gap with an encapsulating polymer adhesive, as is done in the prior art.

20 An improved flip-chip process involves a single-step chip placement followed by solder reflow without the labor intensive underfill encapsulation steps. This improved process is possible if, prior to soldering, the bumped chips or substrate can be coated with a thick layer of the instant invention fluxing composition so that it effectively fluxes the soldering of the
25 interconnections then also hardens to form the solid encapsulant after soldering. The heat applied during the solder reflowing operation will also harden the adhesive to create a high-strength bond.

Attachment of a substrate to a device is illustrated in Figure 1 wherein a flip chip 130 containing solder bumps 140 is positioned so that the solder bumps 140 and the active surface 150 are facing the substrate 100 and aligned with the metallization pattern 110 of the substrate 100. The thermally curable adhesive flux composition 120 is coated on the surface of the substrate and metallization pattern. Referring to Figure 2, the bumped chip 230 is moved into intimate contact with the metallization pattern 210. The thermally curable adhesive flux composition 220 wets the chip 230, insuring complete coverage of the active surface 250 of the chip 230. The fillet 260 provides a continuous seal around the periphery of the chip 230 to protect the active surface 250 from environmental contamination. The fluxing agent contained in composition 220 coats the solder bumps 240 and the metallization pattern 210. The assembly 270 is reflowed in a conventional manner such as in an oven, causing the carboxylic acid in the fluxing agent of the composition to become reactive, reducing the oxides on the solder 240 and the metallization surface 210, and permitting alloying of the solder to the metal. After the reflow process, the fluxing agent in composition 220 and the other crosslinkable carbon-carbon double bonds in the composition, if present, crosslink to one another, hardening the composition to a solid form. Depending on the composition, a second hardening operation may be required by application of additional heat to completely harden the composition 220. During the reflow and hardening steps, the assembly is encapsulated by the composition. Since the encapsulant provides a continuous seal to protect the active surface 250 from environmental contamination, no further cleaning or encapsulating operations are required.

It should be appreciated that although the drawings depict the encapsulation and connection of a flip chip 130 to a substrate, embodiments using other types of surface mounted components, cables, or connectors having solder bumps are within the scope of the invention. Similarly, instead of solder

bumps, a solder paste comprising a solder powder and the thermally curable adhesive composition can be employed. Suitable solder powders comprise, for example, tin/lead, tin/lead/silver, and tin/lead/antimony solder powders. The inventive thermally curable adhesive composition is also suitable for soldering
5 and mechanically attaching a flat cable to a printed circuit or flat panel display without the need for a separate connector.

Another assembly technique involves formulating a curable adhesive composition which is solid at room temperature, but melts without crosslinking at an elevated temperature, e.g. Example 5. As shown in Figure 3, the molten
10 curable adhesive composition 320 can be first applied to the solder bumped chip 130 and allowed to cool and harden to form a chip/adhesive/bump subassembly. This subassembly can be applied to the substrate 100 with or without addition of any other flux. A small amount of heat may be used to soften the composition 320 so that it holds the chip 230 in place until the solder is
15 reflowed as shown in Figure 4. If allowed to cool, this molten composition 320 can temporarily support the chip 230 in place for chip testing or burn in. The chip can thus be easily removed should it malfunction. When it is desired to permanently attach the chip, the substrate and subassembly can be passed through a solder reflow oven thereby melting the solder bumps 340, activating the flux in composition 420, forming permanent solder joints, and crosslinking
20 the adhesive in the composition as shown in Figure 5.

Another approach to the above involves adding a diluent to a mixture of solid and liquid fluxing agent to create a somewhat sticky mixture. The mixture is applied to the chip by warming as described above, then hardened to
25 form a somewhat pressure-sensitive adhesive. Placement of the chip on the substrate will then hold the chip in place until the solder is reflowed.

As is apparent, the thermally curable adhesive composition can be dispensed on the substrate or the chip prior to performing the solder bump

reflowing. The novel flip-chip attachment process has a number of advantages. For example, during the reflow operation, the composition also hardens and encapsulates the flip chip assembly. This eliminates the additional steps of reflowing the solder bump and then underfilling and curing the encapsulant that results in reduced production efficiency in prior art processes. In addition, there is no need to underfill any material into the tiny gap in the flip chip assembly. Void formation from the underfilling procedure and separation of the polymer from the ceramic fillers during application in prior art processes are eliminated. The flux residues remaining in the gap are not only rendered harmless, but also become integral to the structure of the final assembly. Finally, there is no longer a size limit on the chip that can be attached.

To achieve these advantages, the inventive thermally curable composition exhibit the following features:

- a) provides sufficient flux activity to promote the solder bump to readily wet the metallization on the substrate during solder reflow, without the presence of corrosive flux activators that can contaminate the silicon chip;
- b) promotes solder wetting and self-alignment of the chip to the pads on the substrate by action of the wetting force of the molten solder, during the solder reflow cycle, no hardening of the flux composition occurs until the solder bump has been melted;
- c) reduces or eliminates gaseous evolution during the reflow cycle that would otherwise create voids;
- d) hardens quickly and soon after solder bump melts;
- e) demonstrates little shrinkage of the composition during hardening to minimize the stress resulting from the hardening process and subsequent cooling;
- f) after cure, provides high electrical insulation resistance even in humid and hot environments; and

g) forms strong adhesion of the cured composition to the chip, substrate and solder joints.

EXPERIMENTAL

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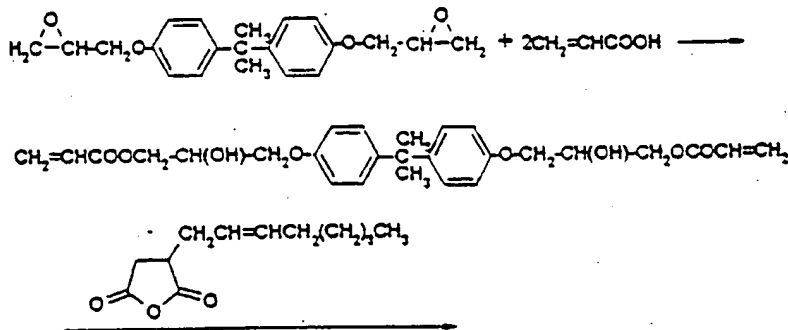
EXAMPLE 1

Preparation of bisphenol A glycerolate di(2-octen-1-ylsuccinic) acid monoester

10.54 g of bisphenol A diglycidyl ether was heated to 70°C under stirring and then 4.46 g acrylic acid was added slowly under nitrogen atmosphere. After maintaining the reaction at 70°C for 2 hours, 13.0 g of 2-octen-1-ylsuccinic anhydride was added and then the temperature was raised to 80°C under mechanical stirring. The reactants are stirred at 80°C for 2-3 hours to complete the reaction.

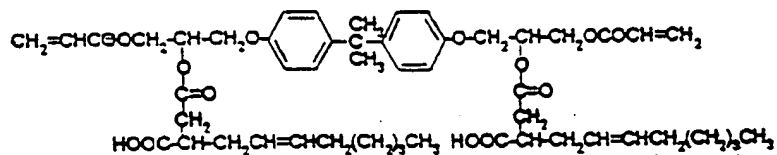
The reactions involved in this synthesis include:

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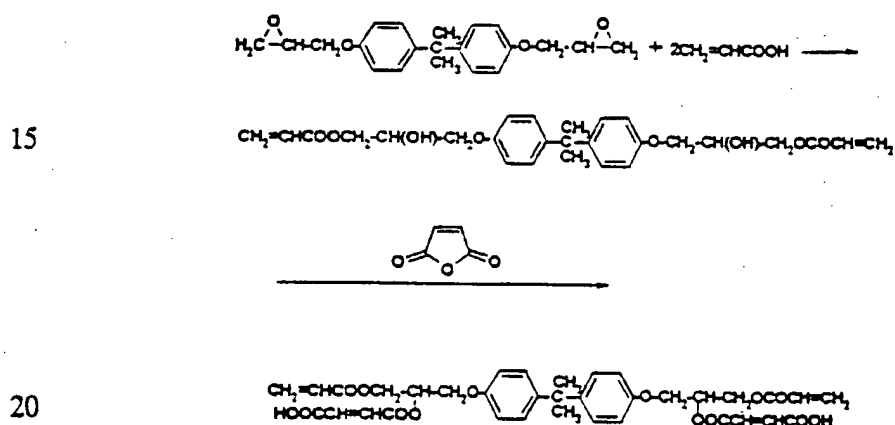


EXAMPLE 2

Preparation of bisphenol A diglycerolate dimaleic acid monoester

34.8 g of bisphenol A diglycidyl ether was heated to 70°C under continuous stirring and then 14.4 g of acrylic acid was added slowly under nitrogen atmosphere. After maintaining the reaction at 70°C for 2 hours, 19.6 g of maleic anhydride was added and then the temperature was raised to 80°C under mechanical stirring for 2-3 hours to complete the reaction.

The reaction involved in this synthesis is:

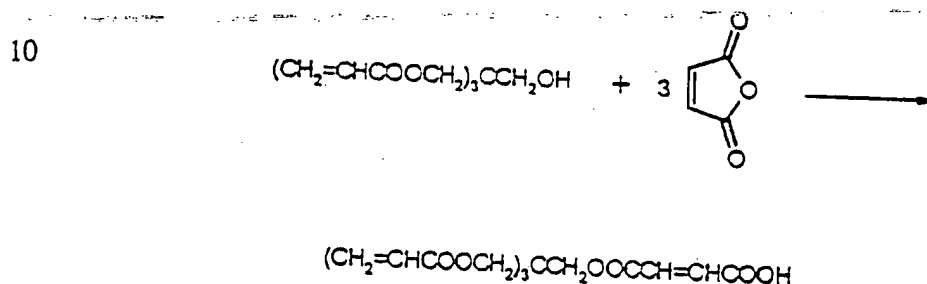


EXAMPLE 3

Synthesis of pentaerythritol triacrylate maleic acid monoester

9.8 g of maleic anhydride was heated to 80°C under nitrogen atmosphere until all the maleic anhydride is melted before 29.8 g of pentaerythritol triacrylate was added slowly under continuous stirring. The reaction was then maintained at 80°C for 3 hours followed by cooling to room temperature.

The reaction involved in this synthesis is:

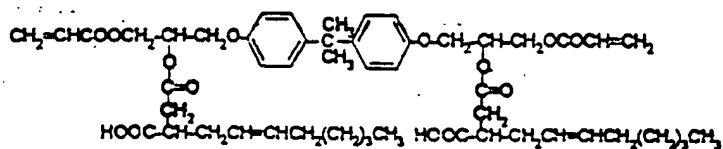


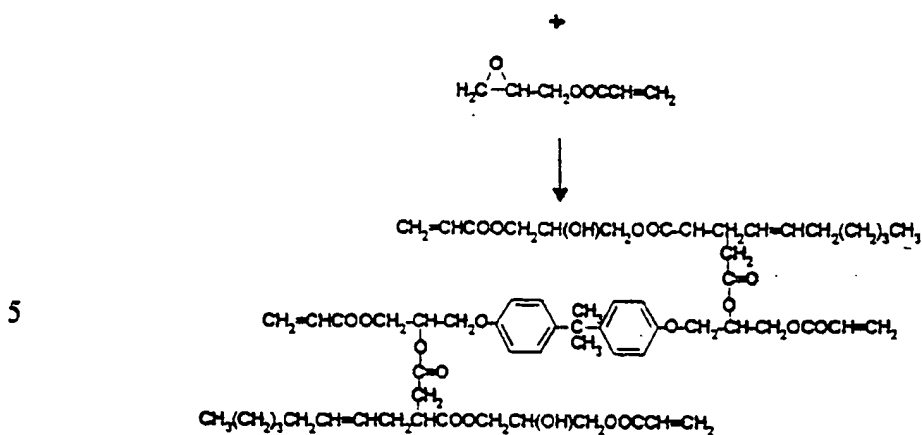
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EXAMPLE 4

20 Formulation of fluxing adhesive

Stoichiometric amounts of glycidyl methacrylate was added to the flux agent to neutralize the carboxyl groups. 24.6 g of glycidyl methacrylate was added to 75.4 g of bisphenol A glycerolate di(2-octen-1-ylsuccinic) acid monoester and the mixture was thoroughly stirred at 60°C for 10 min. The reaction that occurs after reflow is:

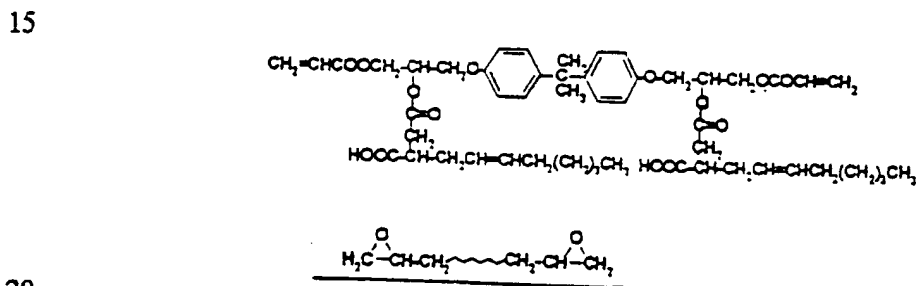




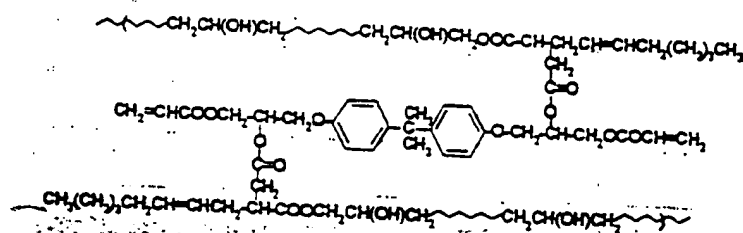
EXAMPLE 5

Formulation of fluxing adhesive

10 Stoichiometric amounts of bisphenol A based epoxy was added to the flux agent to neutralize the carboxyl groups. 30.3 g bisphenol A based epoxy was added to 71.5 g bisphenol A glycerolate di(2-octen-1-ylsuccinic) acid monoester and the mixture was thoroughly stirred at 60°C for 10 min. The reaction that occurs after reflow is:



20



EXAMPLE 6

Formulation of fluxing adhesive

15.3 g bisphenol A based epoxy and 10 g glycidyl methacrylate was
5 added to 74.5 g bisphenol-A glycerolate di(2-octen-1-ylsuccinic) acid monoester
and the mixture was thoroughly stirred at 60°C for 10 min. Then the mixture
was cooled to room temperature for use.

EXAMPLE 7

Formulation of fluxing adhesive

10

21.6 g glycidyl methacrylate and 10 g pentaerythritol tetraacrylate was
added to 68.4 g bisphenol A glycerolate di(2-octen-1-ylsuccinic) acid monoester
and the mixture was thoroughly stirred at 60°C for 10 min. The mixture was
cooled to room temperature for use.

15

EXAMPLE 8

Formulation of fluxing adhesive

21.6 g glycidyl methacrylate and 10 g pentaerythritol tetraacrylate was
20 added to 68.4 g bisphenol A glycerolate dimaleic acid monoester and the
mixture was thoroughly stirred at 60°C for 10 min. The mixture was cooled to
room temperature for use.

EXAMPLE 9

25

The inventive compositions were formulated as follows:

	% Fluxing Agent in Composition Number:					
Fluxing Agent	1	2	3	4	5	6

bisphenol A glycerolate di(2- octen-1-ylsuccinic) acid monoester	100	70	75	75	60	65
bisphenol A diglycidyl ether	--	30	--	15	40	25
glycidyl methacrylate	--	--	25	10	--	--
pentaerythritol tetraacrylate	--	--	--	--	--	10

Physical characteristics of the inventive curable adhesive compositions were measured. The results are set forth in the following table. SIR is surface insulation resistance.

Composition	Solder Spread (Area)	Glass Transition Temperature Tg(°C)	Thermal Degradation Temperature (°C)	SIR (Ohms) (85°C, 85%RH after 168 Hrs.)	Shear strength for gold surfaced (Mpa)	Shear strength after 110 Hrs. humidity (85°C, 85% RH)
A	1.28	--	--	--	--	--
1	3.80	>200	>350	2.28E8	20.57	--
2	3.45	>200	>270	2.35E8	30.16	--
3	3.62	>200	>300	2.42E8	22.31	36.31
4	3.56	>200	>320	2.30E8	33.84	35.42
5	3.27	>200	>290	2.46E8	32.94	44.86
6	3.25	>200	>300	2.25E8	28.62	32.58

Composition A consisted of an adhesive material that is described in U.S. Patent No. 5,128,746 (Example 4) which contains a fluxing agent and hardener. The composition was prepared with the following components (by

weight): 50% Shell EPON 825 epoxy resin (Shell Chemical Co.), 7% malic acid, 42% methylhexahydrophthalic anhydride (MA) and 1% imidazole. The malic acid and the epoxy resin were mixed and heated to about 150°C with stirring until the solution was clear. The solution was allowed to cool to room temperature before the MA and imidazole were added and the mixture was stirred until uniform.

As is apparent, the inventive compositions yield superior physical properties. The solder spread was measured by placing a ball of solder on a surface and then applying a small amount of the curable adhesive composition (or composition A) to the solder. The surface was then heated to about 200°C and the area that the melted solder covered was measured. The solder spread values are normalized, that is, the solder spread in the case where no fluxing agent was employed is equal to 1.

The surface insulation resistance (SIR) test was performed according to the IPC-TM-650 test method and using the IPC-B-24 test board, both available from the IPC, Lincolnwood, Ill. The test was conducted at 85°C and 20% relative humidity at the start. The chamber is stabilized under these conditions for 3 hours, then the humidity is slowly increased to 85% over a 15 minute period and the specimens were allowed to come to equilibrium for at least 1 hour before applying a bias voltage. The bias voltage for this test is 50 v. The test voltage is -100 v. Insulation resistance is measured at the start and at 168 hours. Using this test method, all the formulations listed above exhibited significantly lower insulation resistance values if prepared without a carboxylic acid neutralizing agent. Many test boards made with the above formulations, but without the neutralizing agent exhibited electromigration.

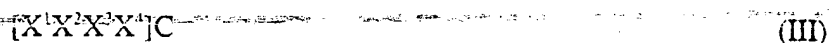
Although only preferred embodiments of the invention are specifically disclosed and described above, it will be appreciated that many modifications and variations of the present invention are possible in light of the above

teachings and within the purview of the appended claims without departing from the spirit and intended scope of the invention.

What is Claimed is:

1. A thermally curable adhesive composition that comprises:

- (a) a fluxing agent that comprises a carboxyl group and that
 5 is selected from the group consisting of compounds represented by Formulae I, II, and III, and mixtures thereof,



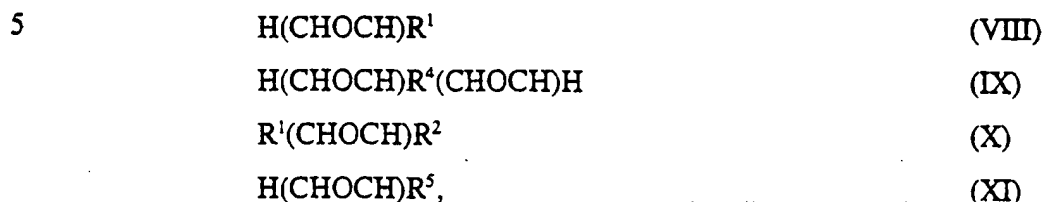
- 10 wherein R^{18} is an alkyl having 1 to 16 carbons, wherein n is an integer from 1 to 16, wherein each of R^1 , R^2 , ... R^n , is independently selected from $-\text{C}(\text{O})\text{CH}=\text{CHCOOH}$, and H, wherein X^1 , X^2 , X^3 , and X^4 , are each independently selected from $-\text{CH}_2\text{OH}$, $-\text{CH}_2\text{OC}(\text{O})\text{CH}=\text{CHCOOH}$, and H, with the proviso that not all of X^1 , X^2 , X^3 , and X^4 are H:

- 15 (b) a carboxylic acid neutralizing agent;
 (c) optionally, an effective amount of a diluent;
 (d) optionally, an effective amount of a source of free radical
 initiators; and
 (e) optionally, an effective amount of a resin.

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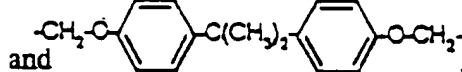
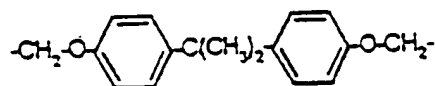
2. The thermally curable adhesive composition of claim 1 wherein the carboxylic acid neutralizing agent comprises a compound that has the structure $\text{R}^1\text{-X-R}^2$, wherein X is a functional group that is selected from an epoxide, $-\text{NH}-$, $-\text{CH}(\text{OH})-$, and mixtures thereof, wherein R^1 and R^2 are
 25 independently selected from (i) H, (ii) alkyl or alkylene moiety having 1 to 18 carbons and (iii) aromatic moiety, and mixtures thereof.

3. The thermally curable adhesive composition of claim 1 wherein the carboxylic acid neutralizing agent comprises a compound that is selected from the group consisting of compounds represented by Formulae VIII, IX, X, and XI, and mixtures thereof,



wherein R^1 and R^2 are independently selected from (i) H, (ii) alkyl or alkylene moiety having 1 to 18 carbons and (iii) aromatic moiety, and mixtures thereof, and wherein R^4 is selected an alkyl, alkylene, aromatic group, and mixtures thereof, and wherein R^5 comprises a moiety having one or more carbon-carbon double bonds.

15 4. The thermally curable adhesive composition of claim 3 wherein R^1 , R^2 , and R^4 is selected from the group consisting of $\text{CH}_2=\text{C}(\text{CH}_3)\text{COOCH}_2$ -,



20 and mixtures thereof, and wherein R^5 contains at least one acrylate ($-\text{C}(\text{O})\text{CH}=\text{CH}_2$) or methacrylate ($-\text{C}(\text{O})\text{C}(\text{CH}_3)=\text{CH}_2$) group.

5. The thermally curable adhesive composition of claim 1 wherein the fluxing agent is selected from the group consisting of bisphenol A glycerolate di(2-octen-1-lysuccinic) acid monoester and bisphenol A diglycerolate dimaleic-acid monoester and the carboxylic acid neutralizing agent is selected from glycidyl methacrylate and bisphenol A epoxy.

6. A thermally curable adhesive composition that comprises:

(a) a fluxing agent that comprises a carboxyl group and that is selected from the group consisting of compounds represented by Formulae IV, V, VI and mixtures thereof,



where R'^{18} is a substituted alkyl moiety containing at least one acrylate or methacrylate moiety and said substituted alkyl moiety comprising a chain
 10 having 1 to 16 carbons, and wherein n is an integer from 1 to 16, wherein each of R'^1 , R'^2 , ..., R'^n , is independently selected from $-\text{C}(\text{O})\text{CH}=\text{CHCOOH}$, $-\text{C}(\text{O})\text{CH}=\text{CH}_2$, $-\text{C}(\text{O})\text{C}(\text{CH}_3)=\text{CH}_2$, and H, and wherein Y^1 , Y^2 , Y^3 , and Y^4 , are each independently selected from $-\text{CH}_2\text{OH}$, $-\text{CH}_2\text{OCOCH}=\text{CH}_2$, $-\text{CH}_2\text{OCOC}(\text{CH}_3)=\text{CH}_2$, $-\text{CH}_2\text{OC}(\text{O})\text{CH}=\text{CHCOOH}$ and H with the proviso
 15 that not all Y^1 , Y^2 , Y^3 , and Y^4 are H;

(b) a carboxylic acid neutralizing agent;

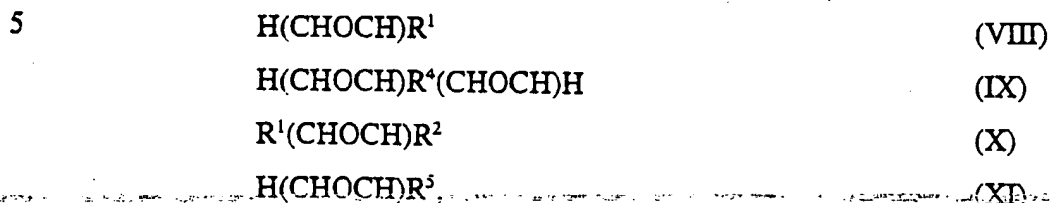
(c) optionally, an effective amount of a diluent;

(d) optionally, an effective amount of a source of free radical initiators; and

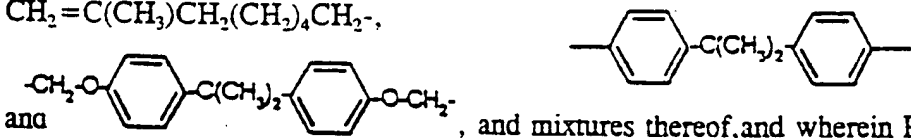
20 (e) optionally, an effective amount of a resin.

7. The thermally curable adhesive composition of claim 6 wherein the carboxylic acid neutralizing agent comprises a compound that has the structure $\text{R}^1\text{-X-R}^2$, wherein X is a functional group that is selected from an
 25 epoxide, $-\text{NH}-$, $-\text{CH}(\text{OH})-$, and mixtures thereof, wherein R^1 and R^2 are independently selected from (i) H, (ii) alkyl or alkylene moiety having 1 to 18 carbons and (iii) aromatic moiety, and mixtures thereof.

8. The thermally curable adhesive composition of claim 5 wherein the carboxylic acid neutralizing agent comprises a compound that is selected from the group consisting of compounds represented by Formulae VIII, IX, X, and XI, and mixtures thereof,



wherein R^1 and R^2 are independently selected from (i) H, (ii) alkyl or alkylene moiety having 1 to 18 carbons and (iii) aromatic moiety, and mixtures thereof, and wherein R^4 is selected an alkyl, alkylene, aromatic group, and mixtures thereof, and wherein R^5 comprises a moiety having one or more carbon-carbon double bonds.

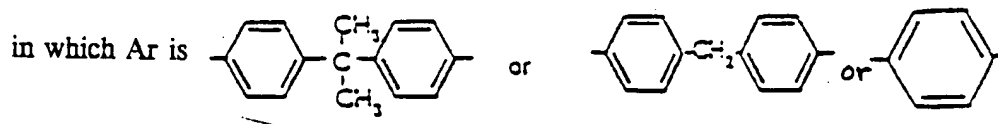
15 9. The thermally curable adhesive composition of claim 8 wherein R^1 , R^2 , and R^4 is selected from the group consisting of $\text{CH}_2=\text{C}(\text{CH}_3)\text{COOCH}_2-$, $\text{CH}_2=\text{C}(\text{CH}_3)\text{CH}_2(\text{CH}_2)_4\text{CH}_2-$,

 and mixtures thereof, and wherein R^5
 20 contains at least one acrylate ($-\text{C}(\text{O})\text{CH}=\text{CH}_2$) or methacrylate ($-\text{C}(\text{O})\text{C}(\text{CH}_3)=\text{CH}_2$) group.

10. The thermally curable adhesive composition of claim 6 wherein the fluxing agent is selected from the group consisting of bisphenol A
 25 glycerolate di(2-octen-1-ylsuccinic) acid monoester and bisphenol A diglycerolate dimaleic acid monoester and the carboxylic acid neutralizing agent is selected from glycidyl methacrylate and bisphenol A epoxy.

11. A thermally curable adhesive composition that comprises:

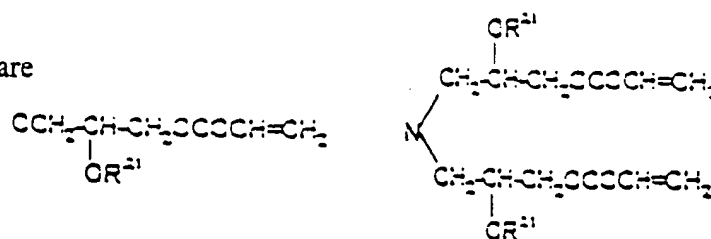
- (a) a fluxing agent that comprises a carboxyl group and R^{19} -Ar- R^{20} (VIII)

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and R^{19} and R^{20} are



15 in which R^{21} is $-C(O)CH=CH-COOH$, $-C(O)CF_2CF_2COOH$, or H;

- (b) a carboxylic acid neutralizing agent;
 (c) optionally, an effective amount of a diluent;
 (d) optionally, an effective amount of a source of free radical
 20 initiators; and
 (e) optionally, an effective amount of a resin.

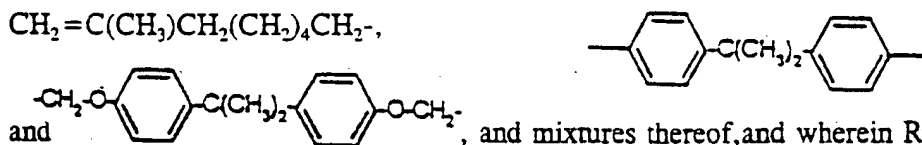
12. The thermally curable adhesive composition of claim 11 wherein
 the carboxylic acid neutralizing agent comprises a compound that has the
 structure R^1 -X- R^2 , wherein X is a functional group that is selected from an
 25 epoxide, $-NH-$, $-CH(OH)-$, and mixtures thereof, wherein R^1 and R^2 are
 independently selected from (i) H, (ii) alkyl or alkylene moiety having 1 to 18
 carbons and (iii) aromatic moiety, and mixtures thereof.

13. The thermally curable adhesive composition of claim 11 wherein the carboxylic acid neutralizing agent comprises a compound that is selected from the group consisting of compounds represented by Formulae VIII, IX, X, and XI, and mixtures thereof,

- 5 $\text{H}(\text{CHOCH})\text{R}^1$ (VIII)
 $\text{H}(\text{CHOCH})\text{R}^4(\text{CHOCH})\text{H}$ (IX)
 $\text{R}^1(\text{CHOCH})\text{R}^2$ (X)
 $\text{H}(\text{CHOCH})\text{R}^5$, (XI)

wherein R^1 and R^2 are independently selected from (i) H, (ii) alkyl or alkylene moiety having 1 to 18 carbons and (iii) aromatic moiety, and mixtures thereof, and wherein R^4 is selected an alkyl, alkylene, aromatic group, and mixtures thereof, and wherein R^5 comprises a moiety having one or more carbon-carbon double bonds.

14. The thermally curable adhesive composition of claim 13 wherein R^1 , R^2 , and R^4 is selected from the group consisting of $\text{CH}_2=\text{C}(\text{CH}_3)\text{COOCH}_2-$, $\text{CH}_2=\text{C}(\text{CH}_3)\text{CH}_2(\text{CH}_2)_4\text{CH}_2-$,



contains at least one acrylate ($-\text{C}(\text{O})\text{CH}=\text{CH}_2$) or methacrylate ($-\text{C}(\text{O})\text{C}(\text{CH}_3)=\text{CH}_2$) group.

15. The thermally curable adhesive composition of claim 11 wherein the fluxing agent is selected from the group consisting of bisphenol A glycerolate di(2-octen-1-ylsuccinic) acid monoester and bisphenol A diglycerolate dimaleic acid monoester and the carboxylic acid neutralizing agent is selected from glycidyl methacrylate and bisphenol A-epoxy.

16. An electrical component assembly, comprising:

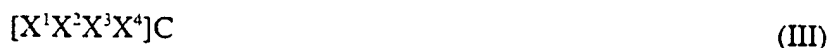
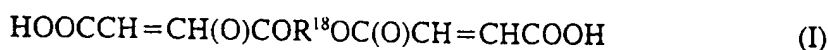
(a) an electrical component having a plurality of electrical terminations;

5 (b) a component carrying substrate having a plurality of electrical terminations corresponding to the terminations of the electrical component; and

(c) a thermally curable adhesive composition that comprises:

(i) a fluxing agent that comprises a carboxyl group

10 and that is selected from the group consisting of compounds represented by Formulae I, II, and III, and mixtures thereof,



15 wherein R^{18} is an alkyl having 1 to 16 carbons, wherein n is an integer from 1 to 16, wherein each of R^1 , R^2 , ..., R^n , is independently selected from $-\text{C}(\text{O})\text{CH}=\text{CHCOOH}$, and H , wherein X^1 , X^2 , X^3 , and X^4 , are each independently selected from $-\text{CH}_2\text{OH}$, $-\text{CH}_2\text{OC}(\text{O})\text{CH}=\text{CHCOOH}$, and H , with the proviso that not all of X^1 , X^2 , X^3 , and X^4 are H ;

20 (ii) a carboxylic acid neutralizing agent;

(iii) optionally, an effective amount of a diluent;

(iv) optionally, an effective amount of a source of free radical initiators; and

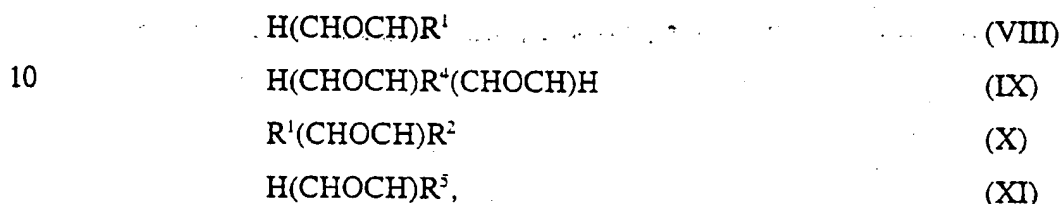
(v) optionally, an effective amount of a resin.

25

17. The electrical component assembly of claim 16 wherein the carboxylic acid neutralizing agent comprises a compound that has the structure $\text{R}^1\text{-X-R}^2$, wherein X is a functional group that is selected from an epoxide, -

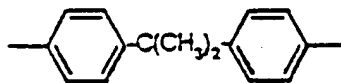
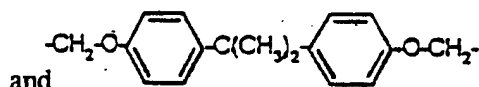
NH-, -CH(OH)-, and mixtures thereof, wherein R¹ and R² are independently selected from (i) H, (ii) alkyl or alkylene moiety having 1 to 18 carbons and (iii) aromatic moiety, and mixtures thereof.

- 5 18. The electrical component of assembly claim 16 wherein the carboxylic acid neutralizing agent comprises a compound that is selected from the group consisting of compounds represented by Formulae VIII, IX, X, and XI, and mixtures thereof.



wherein R¹ and R² are independently selected from (i) H, (ii) alkyl or alkylene moiety having 1 to 18 carbons and (iii) aromatic moiety, and mixtures thereof, and wherein R⁴ is selected an alkyl, alkylene, aromatic group, and mixtures thereof, and wherein R⁵ comprises a moiety having one or more carbon-carbon double bonds.

- 20 19. The electrical component assembly of claim 18 wherein R¹, R², and R⁴ is selected from the group consisting of CH₂=C(CH₃)COOCH₂-,



25 , and mixtures thereof, and wherein R⁵ contains at least one acrylate (-C(O)CH=CH₂) or methacrylate (-C(O)C(CH₃)=CH₂) group.

- 20 20. The electrical component assembly of claim 16 wherein the fluxing agent is selected from the group consisting of bisphenol A glycerolate

di(2-octen-1-ylsuccinic) acid monoester and bisphenol A diglycerolate dimaleic acid monoester and the carboxylic acid neutralizing agent is selected from glycidyl methacrylate and bisphenol A epoxy.

- 5 21. An electrical component assembly, comprising:
- (a) an electrical component having a plurality of electrical terminations;
- (b) a component carrying substrate having a plurality of electrical terminations corresponding to the terminations of the electrical
- 10 component; and
- (c) a thermally curable adhesive composition that comprises:
- (i) a fluxing agent that comprises a carboxyl group and that is selected from the group consisting of compounds represented by Formulae IV, V, VI and mixtures thereof.
- 15
$$\text{HOOCCH}=\text{CH}(\text{O})\text{COR}'^{18}\text{OC}(\text{O})\text{CH}=\text{CHCOOH} \quad (\text{IV})$$
- $\text{R}'^2\text{H}_2\text{C}(\text{HCOR}'^n)_n\text{CH}_2\text{OR}'^3 \quad (\text{V})$
- $[\text{Y}^1\text{Y}^2\text{Y}^3\text{Y}^4]\text{C} \quad (\text{VI})$
- 20 where R'^{18} is a substituted alkyl moiety containing at least one acrylate or methacrylate moiety and said substituted alkyl moiety comprising a chain having 1 to 16 carbons, and wherein n is an integer from 1 to 16, wherein each of R'^1 , R'^2 , ..., R'^n , is independently selected from $-\text{C}(\text{O})\text{CH}=\text{CHCOOH}$, $-\text{C}(\text{O})\text{CH}=\text{CH}_2$, $-\text{C}(\text{O})\text{C}(\text{CH}_3)=\text{CH}_2$, and H, and wherein Y^1 , Y^2 , Y^3 , and Y^4 , are each independently selected from $-\text{CH}_2\text{OH}$, $-\text{CH}_2\text{OCOCH}=\text{CH}_2$, $-\text{CH}_2\text{OCOC}(\text{CH}_3)=\text{CH}_2$, $-\text{CH}_2\text{OC}(\text{O})\text{CH}=\text{CHCOOH}$ and H with the proviso
- 25 that not all Y^1 , Y^2 , Y^3 , and Y^4 are H;
- (ii) a carboxylic acid neutralizing agent;
- (iii) optionally, an effective amount of a diluent;

(iv) optionally, an effective amount of a source of free radical initiators; and

(v) optionally, an effective amount of a resin.

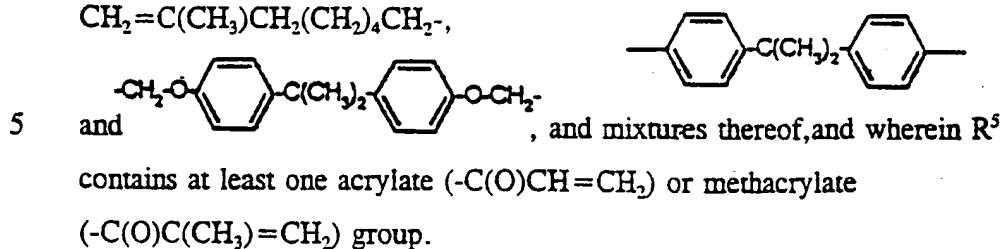
5 22. The electrical component assembly of claim 21 wherein the carboxylic acid neutralizing agent comprises a compound that has the structure R^1-X-R^2 , wherein X is a functional group that is selected from an epoxide, -NH-, -CH(OH)-, and mixtures thereof, wherein R^1 and R^2 are independently selected from (i) H, (ii) alkyl or alkylene moiety having 1 to 18 carbons and
10 (iii) aromatic moiety, and mixtures thereof.

23. The electrical component assembly of claim 21 wherein the carboxylic acid neutralizing agent comprises a compound that is selected from
15 the group consisting of compounds represented by Formulae VIII, IX, X, and XI, and mixtures thereof,



wherein R^1 and R^2 are independently selected from (i) H, (ii) alkyl or alkylene moiety having 1 to 18 carbons and (iii) aromatic moiety, and mixtures thereof, and wherein R^4 is selected an alkyl, alkylene, aromatic group, and mixtures thereof, and wherein R^5 comprises a moiety having one or more carbon-carbon
25 double bonds.

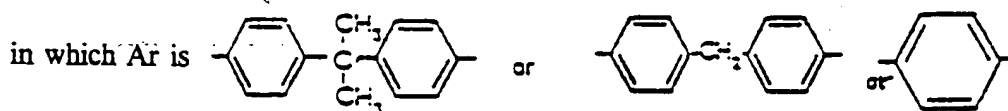
24. The electrical component assembly of claim 23 wherein R^1 , R^2 , and R^4 is selected from the group consisting of $CH_2=C(CH_3)COOCH_2-$, $CH_2=C(CH_3)CH_2(CH_2)_4CH_2-$,



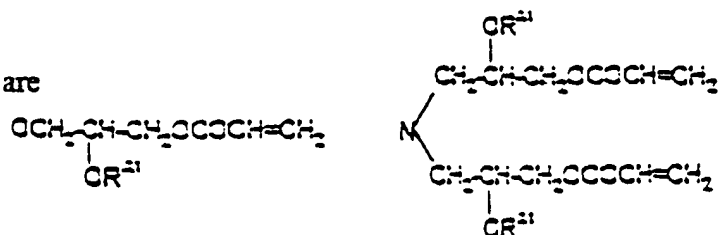
25. The electrical component assembly of claim 21 wherein the
10 fluxing agent is selected from the group consisting of bisphenol A glycerolate di(2-octen-1-ylsuccinic) acid monoester and bisphenol A diglycerolate dimaleic acid monoester and the carboxylic acid neutralizing agent is selected from glycidyl methacrylate and bisphenol A epoxy.

15 26. An electrical component assembly, comprising:
(a) an electrical component having a plurality of electrical terminations;
(b) a component carrying substrate having a plurality of electrical terminations corresponding to the terminations of the electrical
20 component; and
(c) a thermally curable adhesive composition that comprises:
(i) a fluxing agent that comprises a carboxyl group and $R^{19}-Ar-R^{20}$ (VIII)

25



and R¹⁹ and R²⁰ are



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in which R²¹ is -C(O)CH=CH-COOH, -C(O)CF₂CF₂CF₂COOH, or H;

(ii) carboxylic acid neutralizing agent;

(iii) optionally, an effective amount of a diluent;

(iv) optionally, an effective amount of a source of free

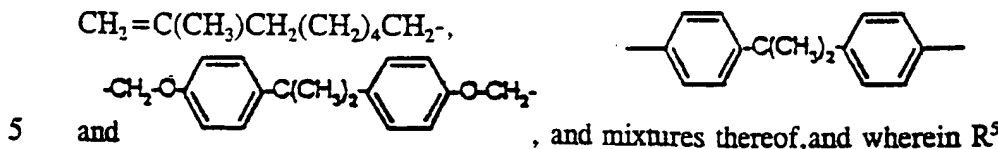
10 radical initiators; and

(v) optionally, an effective amount of a resin.

27. The electrical component assembly of claim 26 wherein the carboxylic acid neutralizing agent comprises a compound that has the structure R¹-X-R², wherein X is a functional group that is selected from an epoxide, -NH-, -CH(OH)-, and mixtures thereof, wherein R¹ and R² are independently selected from (i) H, (ii) alkyl or alkylene moiety having 1 to 18 carbons and (iii) aromatic moiety, and mixtures thereof.

28. The electrical component of assembly claim 26 wherein the carboxylic acid neutralizing agent comprises a compound that has the structure R¹-X-R², wherein X is a functional group that is selected from an epoxide, -NH-, -CH(OH)-, and mixtures thereof, wherein R¹ and R² are independently selected from (i) H, (ii) alkyl or alkylene moiety having 1 to 18 carbons and (iii) aromatic moiety, and mixtures thereof.

29. The electrical component assembly of claim 28 wherein the R¹, R², and R⁴ is selected from the group consisting of CH₂=C(CH₃)COOCH₂-, CH₂=C(CH₃)CH₂(CH₂)₄CH₂-,



contains at least one acrylate (-C(O)CH=CH₂) or methacrylate (-C(O)C(CH₃)=CH₂) group.

30. The electrical component assembly of claim 26 wherein the
10 fluxing agent is selected from the group consisting of bisphenol A glycerolate di(2-octen-1-ylsuccinic) acid monoester and bisphenol A diglycerolate dimaleic acid monoester and the carboxylic acid neutralizing agent is selected from glycidyl methacrylate and bisphenol A epoxy.

15 31. A process for assembling an electronic component that comprises the steps of:

(a) applying a solder and a curable adhesive composition onto component wherein the composition comprises:

20 (i) a fluxing agent that comprises a carboxyl group and that is selected from the group consisting of compounds represented by Formulae I, II, and III, and mixtures thereof,



25 wherein R¹⁸ is an alkyl having 1 to 16 carbons, wherein n is an integer from 1 to 16, wherein each of R¹, R², ...Rⁿ, is independently selected from -C(O)CH=CHCOOH, and H, wherein X¹, X², X³, and X⁴, are each

independently selected from $-\text{CH}_2\text{OH}$, $-\text{CH}_2\text{OC}(\text{O})\text{CH}=\text{CHCOOH}$, and H, with the proviso that not all of X^1 , X^2 , X^3 , and X^4 are H;

(ii) a carboxylic acid neutralizing agent;

(iii) optionally, an effective amount of a diluent;

5 (iv) optionally, an effective amount of a source of free radical initiators;

(v) optionally, an effective amount of a resin; and

(b) heating the solder and fluxing agent to attach the component.

10

32. The process of claim 31 wherein the carboxylic acid neutralizing agent comprises a compound that has the structure $\text{R}^1\text{-X-R}^2$, wherein X is a functional group that is selected from an epoxide, $-\text{NH}-$, $-\text{CH}(\text{OH})-$, and mixtures thereof, wherein R^1 and R^2 are independently selected from (i) H, (ii) 15 alkyl or alkylene moiety having 1 to 18 carbons and (iii) aromatic moiety, and mixtures thereof.

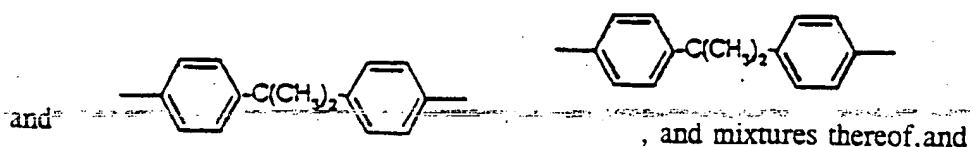
33. The process of claim 31 wherein the carboxylic acid neutralizing agent comprises a compound that is selected from the group consisting of 20 compounds represented by Formulae VIII, IX, X, and XI, and mixtures thereof,



wherein R^1 and R^2 are independently selected from (i) H, (ii) alkyl or alkylene moiety having 1 to 18 carbons and (iii) aromatic moiety, and mixtures thereof,

and wherein R^4 is selected an alkyl, alkylene, aromatic group, and mixtures thereof, and wherein R^5 comprises a moiety having one or more carbon-carbon double bonds.

- 5 34. The process of claim 33 wherein R^1 , R^2 , and R^4 is selected from the group consisting of $\text{CH}_2=\text{C}(\text{CH}_3)\text{COOCH}_2-$, $\text{CH}_2=\text{C}(\text{CH}_3)\text{CH}_2(\text{CH}_2)_4\text{CH}_2-$,

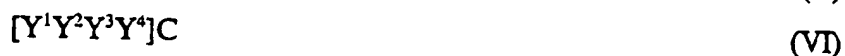
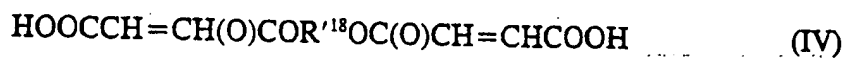


- 10 wherein R^5 contains at least one acrylate ($-\text{C}(\text{O})\text{CH}=\text{CH}_2$) or methacrylate ($-\text{C}(\text{O})\text{C}(\text{CH}_3)=\text{CH}_2$) group.

- 15 35. The process of claim 31 wherein the fluxing agent is selected from the group consisting of bisphenol A glycerolate di(2-octen-1-ylsuccinic) acid monoester and bisphenol A diglycerolate dimaleic acid monoester and the carboxylic acid neutralizing agent is selected from glycidyl methacrylate and bisphenol A epoxy.

- 20 36. A process for assembling an electronic component that comprises the steps of:

- (a) applying a solder and a curable adhesive composition onto component wherein the composition comprises:
- (i) a fluxing agent that comprises a carboxyl group and that is selected from the group consisting of compounds represented by
- 25 Formulae IV, V, VI and mixtures thereof,



where R'^{18} is a substituted alkyl moiety containing at least one acrylate or methacrylate moiety and said substituted alkyl moiety comprising a chain having 1 to 16 carbons, and wherein n is an integer from 1 to 16, wherein each of R'^1, R'^2, \dots, R'^n , is independently selected from $-C(O)CH=CHCOOH$,
 5 $-C(O)CH=CH_2$, $-C(O)C(CH_3)=CH_2$, and H, and wherein Y^1, Y^2, Y^3 , and Y^4 , are each independently selected from $-CH_2OH$, $-CH_2OCOCH=CH_2$, $-CH_2OCOC(CH_3)=CH_2$, $-CH_2OC(O)CH=CHCOOH$ and H with the proviso that not all Y^1, Y^2, Y^3 and Y^4 are H:

- (ii) a carboxylic acid neutralizing agent;
- 10 (iii) optionally, an effective amount of a diluent;
- (iv) optionally, an effective amount of a source of free radical initiators;
- (v) optionally, an effective amount of a resin; and
- (b) heating the solder and fluxing agent to attach the
 15 component.

37. The process of claim 36 wherein the carboxylic acid neutralizing agent comprises a compound that has the structure R^1-X-R^2 , wherein X is a functional group that is selected from an epoxide, $-NH-$, $-CH(OH)-$, and
 20 mixtures thereof, wherein R^1 and R^2 are independently selected from (i) H, (ii) alkyl or alkylene moiety having 1 to 18 carbons and (iii) aromatic moiety, and mixtures thereof.

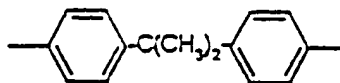
38. The process of claim 36 wherein the carboxylic acid neutralizing
 25 agent comprises a compound that is selected from the group consisting of compounds represented by Formulae VIII, IX, X, and XI, and mixtures thereof,





wherein R^1 and R^2 are independently selected from (i) H, (ii) alkyl or alkylene moiety having 1 to 18 carbons and (iii) aromatic moiety, and mixtures thereof, and wherein R^4 is selected an alkyl, alkylene, aromatic group, and mixtures thereof, and wherein R^5 comprises a moiety having one or more carbon-carbon double bonds.

39. The process of claim 35 wherein the R^1 , R^2 , and R^4 is selected from the group consisting of $\text{CH}_2=\text{C}(\text{CH}_3)\text{COOCH}_2-$,



and $-\text{CH}_2-\text{O}-\text{C}_6\text{H}_4-\text{C}(\text{CH}_3)_2-\text{C}_6\text{H}_4-\text{O}-\text{CH}_2-$, and mixtures thereof, and wherein R^5 contains at least one acrylate ($-\text{C}(\text{O})\text{CH}=\text{CH}_2$) or methacrylate ($-\text{C}(\text{O})\text{C}(\text{CH}_3)=\text{CH}_2$) group.

40. The process of claim 41 wherein the fluxing agent is selected from the group consisting of bisphenol A glycerolate di(2-octen-1-ylsuccinic) acid monoester and bisphenol A diglycerolate dimaleic acid monoester and the carboxylic acid neutralizing agent is selected from glycidyl methacrylate and bisphenol A epoxy.

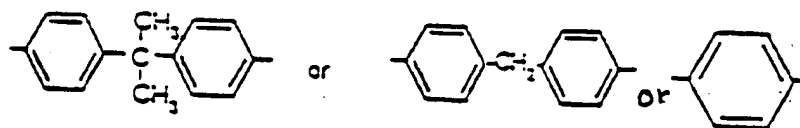
41. A process for assembling an electronic component that comprises the steps of:

(a) applying a solder and a curable adhesive composition onto component wherein the composition comprises:

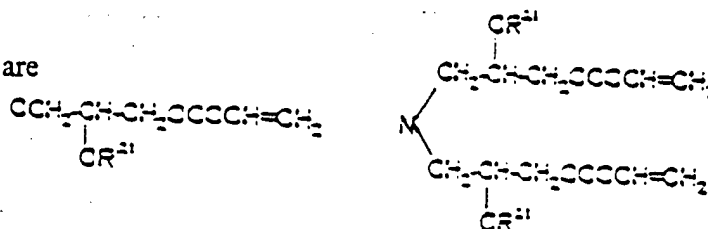
(i) a fluxing agent that comprises a carboxyl group and R^{19} -Ar- R^{20} (VIII)

5

in which Ar is



10 and R^{19} and R^{20} are



in which R^{21} is $-C(O)CH=CH-COOH$, $-C(O)CF_2CF_2CF_2COOH$, or H;

15

- (ii) a carboxylic acid neutralizing agent;
- (iii) optionally, an effective amount of a diluent;
- (iv) optionally, an effective amount of a source of free radical initiators;
- (v) optionally, an effective amount of a resin; and

20

(b) heating the solder and fluxing agent to attach the component.

42. The process of claim 41 wherein the carboxylic acid neutralizing agent comprises a compound that has the structure R^1 -X- R^2 , wherein X is a functional group that is selected from an epoxide, $-NH-$, $-CH(OH)-$, and mixtures thereof, wherein R^1 and R^2 are independently selected from (i) H, (ii) alkyl or alkylene moiety having 1 to 18 carbons and (iii) aromatic moiety, and mixtures thereof.

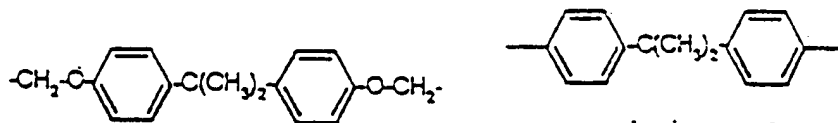
25

43. The process of claim 41 wherein the carboxylic acid neutralizing agent comprises a compound that is selected from the group consisting of compounds represented by Formulae VIII, IX, X, and XI, and mixtures thereof,



wherein R^1 and R^2 are independently selected from (i) H, (ii) alkyl or alkylene moiety having 1 to 18 carbons and (iii) aromatic moiety, and mixtures thereof, and wherein R^4 is selected an alkyl, alkylene, aromatic group, and mixtures thereof, and wherein R^5 comprises a moiety having one or more carbon-carbon double bonds.

44. The process of claim 41 wherein R^1 , R^2 , and R^4 is selected from the group consisting of $\text{CH}_2=\text{C}(\text{CH}_3)\text{COOCH}_2-$, $\text{CH}_2=\text{C}(\text{CH}_3)\text{CH}_2(\text{CH}_2)_4\text{CH}_2-$,



and mixtures thereof, and wherein R^3 contains at least one acrylate ($-\text{C}(\text{O})\text{CH}=\text{CH}_2$) or methacrylate ($-\text{C}(\text{O})\text{C}(\text{CH}_3)=\text{CH}_2$) group.

45. The process of claim 41 wherein the fluxing agent is selected from the group consisting of bisphenol A glycerolate di(2-octen-1-ylsuccinic) acid monoester and bisphenol A diglycerolate dimaleic acid monoester and the carboxylic acid neutralizing agent is selected from glycidyl methacrylate and bisphenol A epoxy.

46. An electrically conductive ink composition formed by curing an adhesive composition comprising:

5 a) 1 to 65% (wt) of a high melting point metal that is selected from the group consisting of Cu, Ag, Au, Pt, Pd, Be, Rh, Ni, Co, Fe, Mo, and alloys thereof;

b) 6 to 65% (wt) of a solder that is selected from the group consisting of Sn, Bi, Pb, Cd, Zn, Ga, In, Hg, Sb, and alloy thereof; and

10 c) 5% to 50% (wt) of the thermally curable adhesive flux composition that comprises:

(i) a fluxing agent that comprises a carboxyl group and that is selected from the group consisting of compounds represented by Formulae I, II, and III, and mixtures thereof.

15 $\text{HOOCCH}=\text{CH}(\text{O})\text{COR}^{18}\text{OC}(\text{O})\text{CH}=\text{CHCOOH}$ (I)

$\text{R}^2\text{H}_2\text{C}(\text{HCOR}^n)_n\text{CH}_2\text{OR}^3$ (II)

$[\text{X}^1\text{X}^2\text{X}^3\text{X}^4]\text{C}$ (III)

wherein R^{18} is an alkyl having 1 to 16 carbons, wherein n is an integer from 1 to 16, wherein each of R^1 , R^2 , ..., R^n , is independently selected from
20 $-\text{C}(\text{O})\text{CH}=\text{CHCOOH}$, and H, wherein X^1 , X^2 , X^3 , and X^4 , are each independently selected from $-\text{CH}_2\text{OH}$, $-\text{CH}_2\text{OC}(\text{O})\text{CH}=\text{CHCOOH}$, and H, with the proviso that not all of X^1 , X^2 , X^3 , and X^4 are H;

(ii) a carboxylic acid neutralizing agent;
(iii) optionally, an effective amount of a diluent;
25 (iv) optionally, an effective amount of a source of free radical initiators; and
(v) optionally, an effective amount of a resin.

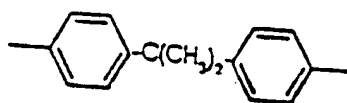
47. The electrically conductive ink composition of claim 46 wherein the carboxylic acid neutralizing agent comprises a compound that has the structure R^1-X-R^2 , wherein X is a functional group that is selected from an epoxide, -NH-, -CH(OH)-, and mixtures thereof, wherein R^1 and R^2 are
 5 independently selected from (i) H, (ii) alkyl or alkylene moiety having 1 to 18 carbons and (iii) aromatic moiety, and mixtures thereof.

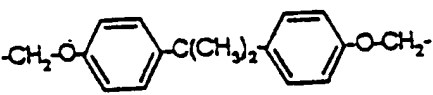
48. The electrically conductive ink composition of claim 46 wherein the carboxylic acid neutralizing agent comprises a compound that is selected
 10 from the group consisting of compounds represented by Formulae VIII, IX, X, and XI, and mixtures thereof,



wherein R^1 and R^2 are independently selected from (i) H, (ii) alkyl or alkylene moiety having 1 to 18 carbons and (iii) aromatic moiety, and mixtures thereof, and wherein R^4 is selected an alkyl, alkylene, aromatic group, and mixtures thereof, and wherein R^5 comprises a moiety having one or more carbon-carbon
 20 double bonds.

49. The electrically conductive ink composition of claim 45 wherein the R^1 , R^2 , and R^4 is selected from the group consisting of $CH_2=C(CH_3)COOCH_2^-$, $CH_2=C(CH_3)CH_2(CH_2)_4CH_2^-$,
 25



and , and mixtures thereof, and wherein R⁵ contains at least one acrylate (-C(O)CH=CH₂) or methacrylate (-C(O)C(CH₃)=CH₂) group.

5 50. The process of claim 46 wherein the fluxing agent is selected from the group consisting of bisphenol A glycerolate di(2-octen-1-ylsuccinic) acid monoester and bisphenol A diglycerolate dimaleic acid monoester and the carboxylic acid neutralizing agent is selected from glycidyl methacrylate and bisphenol A epoxy.

10

51. An electrically conductive ink composition formed by curing an adhesive composition comprising:

a) 1 to 65% (wt) of a high melting point metal that is selected from the group consisting of Cu, Ag, Au, Pt, Pd, Be, Rh, Ni, Co, Fe, Mo, and alloys thereof;

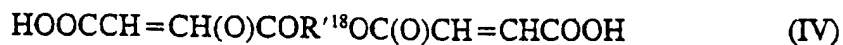
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b) 6 to 65% (wt) of a solder that is selected from the group consisting of Sn, Bi, Pb, Cd, Zn, Ga, In, Hg, Sb, and alloy thereof; and

c) 5% to 50% (wt) of the thermally curable adhesive flux composition that comprises:

20

(i) a fluxing agent that comprises a carboxyl group and that is selected from the group consisting of compounds represented by Formulae IV, V, VI and mixtures thereof,



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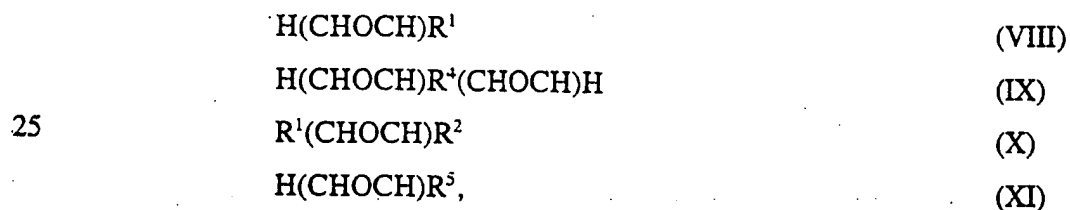
where R'¹⁸ is a substituted alkyl moiety containing at least one acrylate or methacrylate moiety and said substituted alkyl moiety comprising a chain having 1 to 16 carbons, and wherein n is an integer from 1 to 16, wherein each

of $R'^1, R'^2, \dots R'^n$, is independently selected from $-C(O)CH=CHCOOH$,
 $-C(O)CH=CH_2$, $-C(O)C(CH_3)=CH_2$, and H, and wherein Y^1, Y^2, Y^3 , and Y^4 ,
 are each independently selected from $-CH_2OH$, $-CH_2OCOCH=CH_2$,
 $-CH_2OCOC(CH_3)=CH_2$, $-CH_2OC(O)CH=CHCOOH$ and H with the proviso
 5 that not all Y^1, Y^2, Y^3 , and Y^4 are H;

- (ii) a carboxylic acid neutralizing agent;
- (iii) optionally, an effective amount of a diluent;
- (iv) optionally, an effective amount of a source of free
 radical initiators; and
- 10 (v) optionally, an effective amount of a resin.

52. The electrically conductive ink composition of claim 51 wherein
 the carboxylic acid neutralizing agent comprises a compound that has the
 structure R^1-X-R^2 , wherein X is a functional group that is selected from an
 15 epoxide, $-NH-$, $-CH(OH)-$, and mixtures thereof, wherein R^1 and R^2 are
 independently selected from (i) H, (ii) alkyl or alkylene moiety having 1 to 18
 carbons and (iii) aromatic moiety, and mixtures thereof.

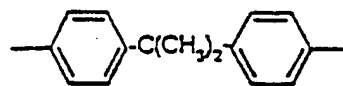
53. The electrically conductive ink composition of claim 51 wherein
 20 the carboxylic acid neutralizing agent comprises a compound that is selected
 from the group consisting of compounds represented by Formulae VIII, IX, X,
 and XI, and mixtures thereof.

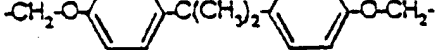


wherein R^1 and R^2 are independently selected from (i) H, (ii) alkyl or alkylene
 moiety having 1 to 18 carbons and (iii) aromatic moiety, and mixtures thereof,

and wherein R^4 is selected an alkyl, alkylene, aromatic group, and mixtures thereof, and wherein R^5 comprises a moiety having one or more carbon-carbon double bonds.

- 5 54. The electrically conductive ink composition of claim 53 wherein the R^1 , R^2 , and R^4 is selected from the group consisting of $CH_2=C(CH_3)COOCH_2-$, $CH_2=C(CH_3)CH_2(CH_2)_4CH_2-$,



- 10 and , and mixtures thereof, and wherein R^5 contains at least one acrylate ($-C(O)CH=CH_2$) or methacrylate ($-C(O)C(CH_3)=CH_2$) group.

- 15 55. The electrically conductive ink composition of claim 51 wherein the fluxing agent is selected from the group consisting of bisphenol A glycerolate di(2-octen-1-ylsuccinic) acid monoester and bisphenol A diglycerolate dimaleic acid monoester and the carboxylic acid neutralizing agent is selected from glycidyl methacrylate and bisphenol A epoxy.

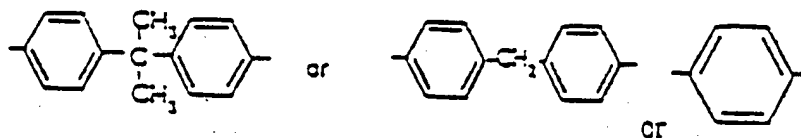
- 20 56. An electrically conductive ink composition formed by curing an adhesive composition comprising:

- a) 1 to 65% (wt) of a high melting point metal that is selected from the group consisting of Cu, Ag, Au, Pt, Pd, Be, Rh, Ni, Co, Fe, Mo, and alloys thereof;
- 25 b) 6 to 65% (wt) of a solder that is selected from the group consisting of Sn, Bi, Pb, Cd, Zn, Ga, In, Hg, Sb, and alloy thereof; and
- c) 5% to 50% (wt) of the thermally curable adhesive flux composition that comprises:

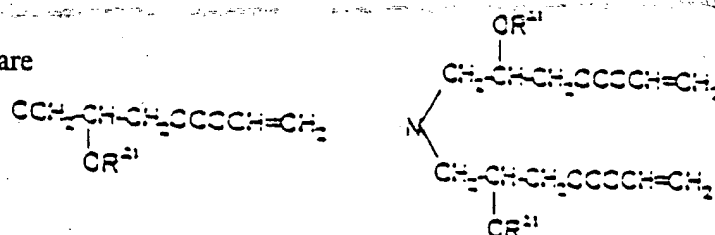
(i) a fluxing agent that comprises a carboxyl group
and R^{19} -Ar- R^{20} (VIII)

5

in which Ar is



10 and R^{19} and R^{20} are



in which R^{21} is $-C(O)CH=CH-COOH$, $-C(O)CF_2CF_2CF_2COOH$, or H;

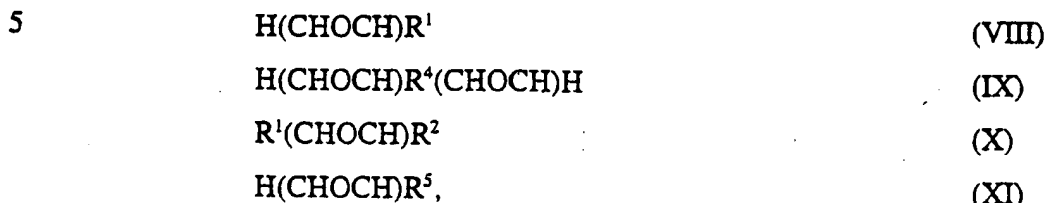
15

- (ii) a carboxylic acid neutralizing agent;
- (iii) optionally, an effective amount of a diluent;
- (iv) optionally, an effective amount of a source of free radical initiators; and
- (v) optionally, an effective amount of a resin.

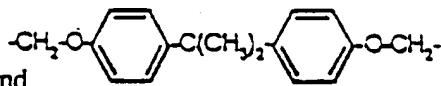
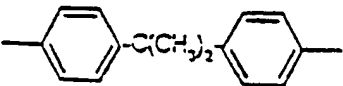
20

57. The electrically conductive ink composition of claim 56 wherein the carboxylic acid neutralizing agent comprises a compound that has the structure R^1 -X- R^2 , wherein X is a functional group that is selected from an epoxide, -NH-, -CH(OH)-, and mixtures thereof, wherein R^1 and R^2 are independently selected from (i) H, (ii) alkyl or alkylene moiety having 1 to 18 carbons and (iii) aromatic moiety, and mixtures thereof.

58. The electrically conductive ink composition of claim 56 wherein the carboxylic acid neutralizing agent comprises a compound that is selected from the group consisting of compounds represented by Formulae VIII, IX, X, and XI, and mixtures thereof,



wherein R^1 and R^2 are independently selected from (i) H, (ii) alkyl or alkylene moiety having 1 to 18 carbons and (iii) aromatic moiety, and mixtures thereof, and wherein R^4 is selected an alkyl, alkylene, aromatic group, and mixtures thereof, and wherein R^5 comprises a moiety having one or more carbon-carbon double bonds.

59. The electrically conductive ink composition of claim 58 wherein R^1 , R^2 , and R^4 is selected from the group consisting of $\text{CH}_2=\text{C}(\text{CH}_3)\text{COOCH}_2-$, $\text{CH}_2=\text{C}(\text{CH}_3)\text{CH}_2(\text{CH}_2)_4\text{CH}_2-$, , , and mixtures thereof, and wherein R^5 contains at least one acrylate ($-\text{C}(\text{O})\text{CH}=\text{CH}_2$) or methacrylate ($-\text{C}(\text{O})\text{C}(\text{CH}_3)=\text{CH}_2$) group.

60. The electrically conductive ink composition of claim 56 wherein the fluxing agent is selected from the group consisting of bisphenol A glycerolate di(2-octen-1-ylsuccinic) acid monoester and bisphenol A diglycerolate dimaleic-acid monoester and the carboxylic acid neutralizing agent is selected from glycidyl methacrylate and bisphenol A epoxy.

61. An electrical component assembly, comprising:

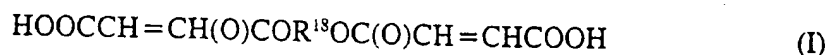
(a) an electrical component having a plurality of electrical terminations;

(b) a component carrying substrate having a plurality of electrical terminations corresponding to the terminations of the electrical component; and

(c) a thermally curable adhesive composition that comprises:

(i) a fluxing agent that comprises a carboxyl group

and that is selected from the group consisting of compounds represented by Formulae I, II, and III, and mixtures thereof,



wherein R^{18} is an alkyl having 1 to 16 carbons, wherein n is an integer from 1 to 16, wherein each of R^1 , R^2 , ..., R^n , is independently selected from $-\text{C}(\text{O})\text{CH}=\text{CHCOOH}$, and H, wherein X^1 , X^2 , X^3 , and X^4 , are each independently selected from $-\text{CH}_2\text{OH}$, $-\text{CH}_2\text{OC}(\text{O})\text{CH}=\text{CHCOOH}$, and H, with the proviso that not all of X^1 , X^2 , X^3 , and X^4 are H;

(ii) a carboxylic acid neutralizing agent;

(iii) optionally, an effective amount of a diluent;

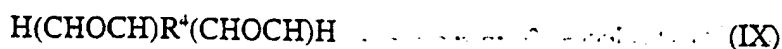
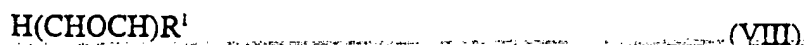
(iv) optionally, an effective amount of a source of free radical initiators; and

(v) optionally, an effective amount of a resin.

62. The electric component assembly of claim 61 wherein the carboxylic acid neutralizing agent comprises a compound that has the structure $\text{R}^1\text{-X-R}^2$, wherein X is a functional group that is selected from an epoxide, $-\text{NH}-$, $-\text{CH}(\text{OH})-$, and mixtures thereof, wherein R^1 and R^2 are independently

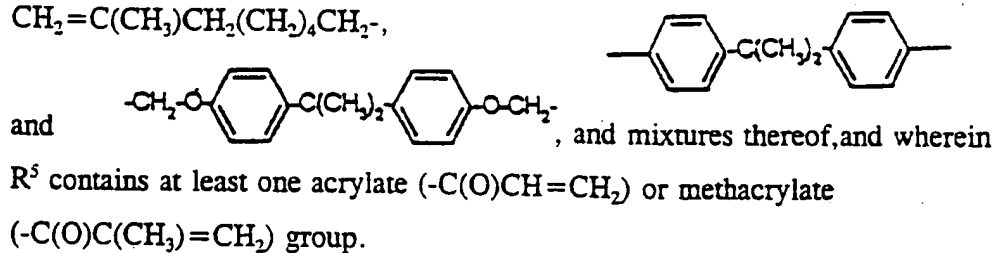
selected from (i) H, (ii) alkyl or alkylene moiety having 1 to 18 carbons and (iii) aromatic moiety, and mixtures thereof.

63. The electric component assembly of claim 61 wherein the
 5 carboxylic acid neutralizing agent comprises a compound that is selected from the group consisting of compounds represented by Formulae VIII, IX, X, and XI, and mixtures thereof,



wherein R^1 and R^2 are independently selected from (i) H, (ii) alkyl or alkylene moiety having 1 to 18 carbons and (iii) aromatic moiety, and mixtures thereof, and wherein R^4 is selected an alkyl, alkylene, aromatic group, and mixtures
 15 thereof, and wherein R^5 comprises a moiety having one or more carbon-carbon double bonds.

64. The electric component assembly of claim 63 wherein R^1 , R^2 , and R^4 is selected from the group consisting of $\text{CH}_2=\text{C}(\text{CH}_3)\text{COOCH}_2-$,
 20 $\text{CH}_2=\text{C}(\text{CH}_3)\text{CH}_2(\text{CH}_2)_4\text{CH}_2-$,



25

65. The electric component assembly of claim 61 wherein the fluxing agent is selected from the group consisting of bisphenol A glycerolate di(2-octen-1-ylsuccinic) acid monoester and bisphenol A diglycerolate dimaleic acid

monoester and the carboxylic acid neutralizing agent is selected from glycidyl methacrylate and bisphenol A epoxy.

- 5 66. An electrical component assembly, comprising:
- (a) an electrical component having a plurality of electrical terminations;
- (b) a component carrying substrate having a plurality of electrical terminations corresponding to the terminations of the electrical
- 10 component; and
- (c) a thermally curable adhesive composition that comprises:
- (i) a fluxing agent that comprises a carboxyl group and that is selected from the group consisting of compounds represented by Formulae IV, V, VI and mixtures thereof,
- 15 $\text{HOOCCH}=\text{CH}(\text{O})\text{COR}'^{18}\text{OC}(\text{O})\text{CH}=\text{CHCOOH}$ (IV)
- $\text{R}'^2\text{H}_2\text{C}(\text{HCOR}'^n)_n\text{CH}_2\text{OR}'^3$ (V)
- $[\text{Y}^1\text{Y}^2\text{Y}^3\text{Y}^4]\text{C}$ (VI)
- where R'^{18} is a substituted alkyl moiety containing at least one acrylate or methacrylate moiety and said substituted alkyl moiety comprising a chain
- 20 having 1 to 16 carbons, and wherein n is an integer from 1 to 16, wherein each of R'^1 , R'^2 , ..., R'^n , is independently selected from $-\text{C}(\text{O})\text{CH}=\text{CHCOOH}$, $-\text{C}(\text{O})\text{CH}=\text{CH}_2$, $-\text{C}(\text{O})\text{C}(\text{CH}_3)=\text{CH}_2$, and H, and wherein Y^1 , Y^2 , Y^3 , and Y^4 , are each independently selected from $-\text{CH}_2\text{OH}$, $-\text{CH}_2\text{OCOCH}=\text{CH}_2$, $-\text{CH}_2\text{OCOC}(\text{CH}_3)=\text{CH}_2$, $-\text{CH}_2\text{OC}(\text{O})\text{CH}=\text{CHCOOH}$ and H with the proviso
- 25 that not all Y^1 , Y^2 , Y^3 , and Y^4 are H;
- (ii) a carboxylic acid neutralizing agent;
- (iii) optionally, an effective amount of a diluent;

- (iv) optionally, an effective amount of a source of free radical initiators; and
- (v) optionally, an effective amount of a resin.

5 67. The electrical component assembly of claim 66 wherein the carboxylic acid neutralizing agent comprises a compound that has the structure R^1-X-R^2 , wherein X is a functional group that is selected from an epoxide, -NH-, -CH(OH)-, and mixtures thereof, wherein R^1 and R^2 are independently selected from (i) H, (ii) alkyl or alkylene moiety having 1 to 18 carbons and

10 (iii) aromatic moiety, and mixtures thereof.

68. The electrical component assembly of claim 66 wherein the carboxylic acid neutralizing agent comprises a compound that is selected from the group consisting of compounds represented by Formulae VIII, IX, X, and

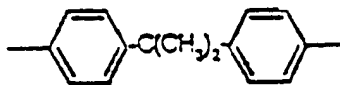
15 XI, and mixtures thereof,



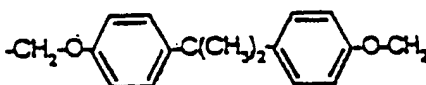
20 wherein R^1 and R^2 are independently selected from (i) H, (ii) alkyl or alkylene moiety having 1 to 18 carbons and (iii) aromatic moiety, and mixtures thereof, and wherein R^4 is selected an alkyl, alkylene, aromatic group, and mixtures thereof, and wherein R^5 comprises a moiety having one or more carbon-carbon double bonds.

25

69. The electrical component assembly of claim 65 wherein R^1 , R^2 , and R^4 is selected from the group consisting of $CH_2=C(CH_3)COOCH_2-$, $CH_2=C(CH_3)CH_2(CH_2)_4CH_2-$,



61

and , and mixtures thereof, and wherein R⁵ contains at least one acrylate (-C(O)CH=CH₂) or methacrylate (-C(O)C(CH₃)=CH₂) group.

5

70. The electrical component assembly of claim 65 wherein the fluxing agent is selected from the group consisting of bisphenol A glycerolate di(2-octen-1-ylsuccinic) acid monoester and bisphenol A diglycerolate dimaleic acid monoester and the carboxylic acid neutralizing agent is selected from glycidyl methacrylate and bisphenol A epoxy.

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71. An electrical component assembly, comprising:

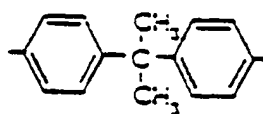
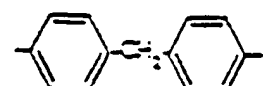
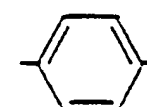
(a) an electrical component having a plurality of electrical terminations;

15 (b) a component carrying substrate having a plurality of electrical terminations corresponding to the terminations of the electrical component; and

(c) a thermally curable adhesive composition that comprises:

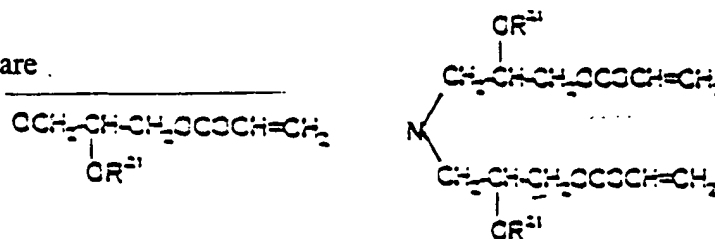
(i) a fluxing agent that comprises a carboxyl group

20 and R¹⁹-Ar-R²⁰ (VIII)

in which Ar is  or  or 

25

and R¹⁹ and R²⁰ are



in which R^{21} is $-C(O)CH=CH-COOH$, $-C(O)CF_2CF_2CF_2COOH$, or H;

- (ii) a carboxylic acid neutralizing agent;
- (iii) optionally, an effective amount of a diluent;
- 5 (iv) optionally, an effective amount of a source of free radical initiators; and
- (v) optionally, an effective amount of a resin.

72. The electrical component assembly of claim 71 wherein the
 10 carboxylic acid neutralizing agent comprises a compound that has the structure R^1-X-R^2 , wherein X is a functional group that is selected from an epoxide, -NH-, -CH(OH)-, and mixtures thereof, wherein R^1 and R^2 are independently selected from (i) H, (ii) alkyl or alkylene moiety having 1 to 18 carbons and (iii) aromatic moiety, and mixtures thereof.

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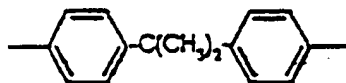
73. The electrical component assembly of claim 71 wherein the carboxylic acid neutralizing agent comprises a compound that is selected from the group consisting of compounds represented by Formulae VIII, IX, X, and XI, and mixtures thereof,

- 20 $H(CHOCH)R^1$ (VIII)
- $H(CHOCH)R^4(CHOCH)H$ (IX)
- $R^1(CHOCH)R^2$ (X)
- $H(CHOCH)R^5$, (XI)

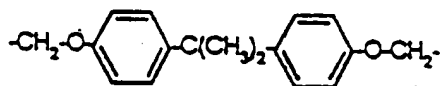
wherein R^1 and R^2 are independently selected from (i) H, (ii) alkyl or alkylene moiety having 1 to 18 carbons and (iii) aromatic moiety, and mixtures thereof,
 25 and wherein R^4 is selected an alkyl, alkylene, aromatic group, and mixtures thereof, and wherein R^5 comprises a moiety having one or more carbon-carbon double bonds.

74. The electrical component assembly of claim 73 wherein R¹, R², and R⁴ is selected from the group consisting of CH₂=C(CH₃)COOCH₂-, CH₂=C(CH₃)CH₂(CH₂)₄CH₂-,

5



and



, and mixtures thereof, and

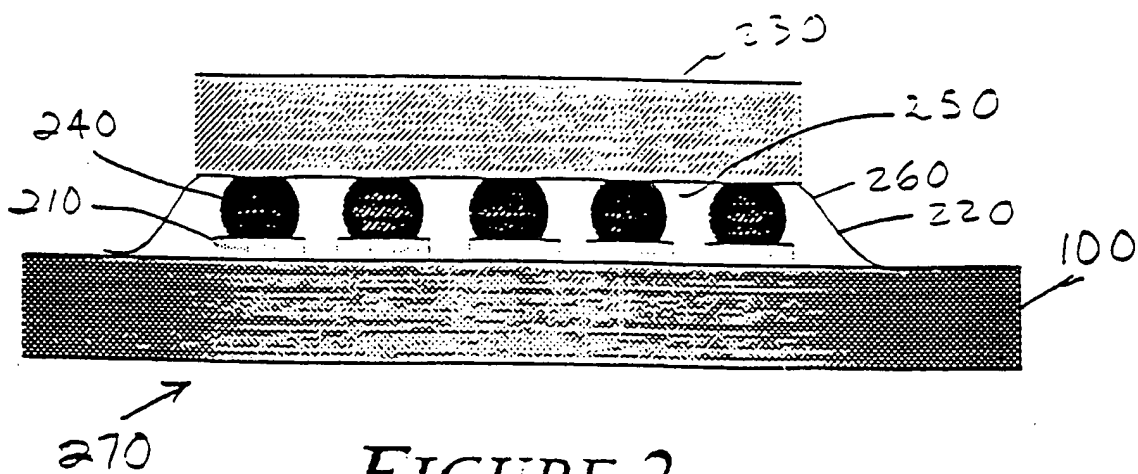
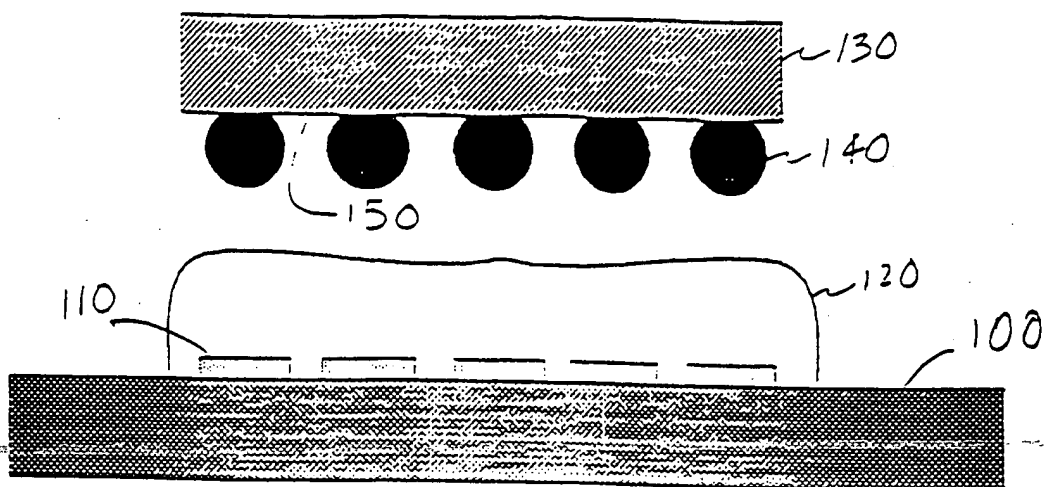
wherein R⁵ contains at least one acrylate (-C(O)CH=CH₂) or methacrylate (-C(O)C(CH₃)=CH₂) group.

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75. The electrical component of claim 71 wherein the fluxing agent is selected from the group consisting of bisphenol A glycerolate di(2-octen-1-ylsuccinic) acid monoester and bisphenol A diglycerolate dimaleic acid monoester and the carboxylic acid neutralizing agent is selected from glycidyl methacrylate and bisphenol A epoxy.

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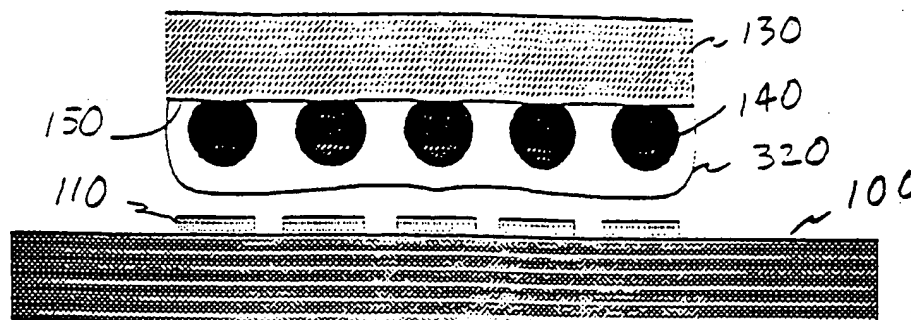


FIGURE 3

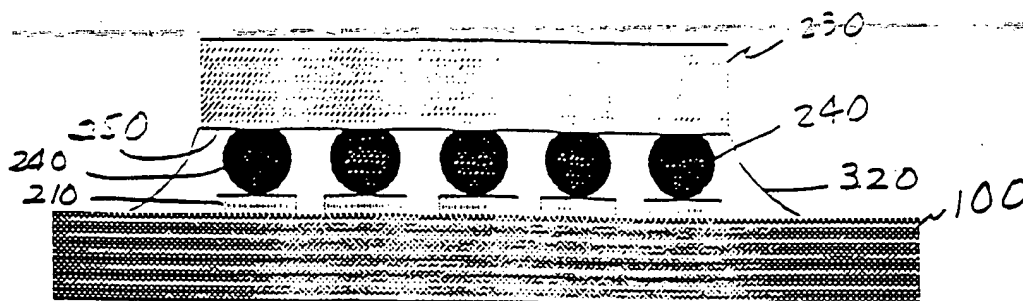


FIGURE 4

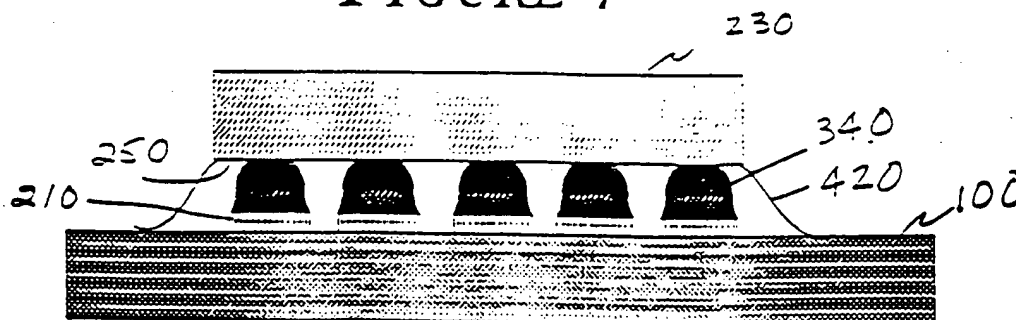


FIGURE 5

INTERNATIONAL SEARCH REPORT

 International application No.
PCT/US98/15031

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : Please See Extra Sheet.

US CL : Please See Extra Sheet.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 427/96, 97, 265, 282, 294; 252/512, 513, 514, 518; 156/277; 148/24, 25; 528/112

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5,538,789 A (CAPOTE et al.) 23 June 1996.	1-75
A	US 5,177,134 A (MULLEN, III et al.) 5 January 1993.	1-75
A	US 4,342,607 A (ZADO) 3 August 1982.	1-75
A	US 4,113,525 A (Stayner et al.) 12 September 1978.	1-75
A	US 3,944,123 A (JACOBS) 16 March 1976.	1-75
A	US 3,877,978 A (KREMEN et al.) 15 April 1975.	1-75



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:	*T*	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
A document defining the general state of the art which is not considered to be of particular relevance	*X*	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
B earlier document published on or after the international filing date	*Y*	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*A*	document member of the same patent family
O document referring to an oral disclosure, use, exhibition or other means		
P document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search

03 NOVEMBER 1998

Date of mailing of the international search report

16 NOV 1998

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Facsimile No. (703) 305-3230

Authorized officer

PETER D. MULCAHY

Telephone No. (703) 308-0664

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US98/15031

A. CLASSIFICATION OF SUBJECT MATTER:

IPC (6):

B05D 5/12; B32B 7/00, 31/00; D04H 1/16, 1/04; H01B 1/02, 1/06; B23K 35/34; C08G 59/40

A. CLASSIFICATION OF SUBJECT MATTER:

US CL :

427/96, 97, 265, 282, 294; 252/512, 513, 514, 518; 156/277; 148/24, 25; 528/112